RADIOTRACER STUDIES OF THE CHLOROFLUORINATION OF SULPHUR TETRAFLUORIDE AT MERCURY(II) FLUORIDE

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BY

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Summary

The room temperature reaction between sulphur tetrafluoride and chlorine monofluoride in the presence of mercury(II) fluoride has been described in this work. Using [^{35}S]- sulphur labelled sulphur tetrafluoride and [^{36}Cl]- chlorine labelled chlorine monofluoride, the catalytic activity of mercury(II) fluoride for the above reaction has been studied.

The interaction between the probe molecules sulphur tetrafluoride or chlorine monofluoride with mercury(II) fluoride under heterogenous conditions has been examined using radiochemically labelled species [^{35}S]- sulphur labelled sulphur tetrafluoride and [^{36}Cl]- chlorine labelled chlorine monofluoride. Possible poisoning reactions resulting from the interaction of these probe molecules with mercury(II) fluoride have also been examined by studying the chemisorption and retention of these molecules at mercury(II) fluoride surface.

It has been shown that preteatment of mercury(II) fluoride before use as a catalyst affects both its catalytical activity and B.E.T area. However, its pretreatment with hexafluoroacetone in the presence of acetonitrile followed by thermal decomposition of its adduct formed, has been found to be the most effective way to increase the B.E.T area and enhance its catalytic actvity. The pretreatment of mercury(II) fluoride with sulphur tetrafluoride has also been used. However the latter method is less effective.

The B.E.T area of mercury(II) fluoride untreated and pretreated has been determined in this work. The radioisotope ^{85}Kr has been used as adsorbate for small B.E.T area determination. However for the large B.E.T area, N_2 has been used as adsorbate.

CHAPTER ONE

CHAPTER ONE

Introduction :

Heterogeneous catalysis has been synonymous with industrial catalysis and the chemical industry for many years. Substances which play an important role in decreasing the activation energy during the reaction process, that is accelerating the chemical reaction, without undergoing any changes, are known as catalysts[1].

Adsorption processes are fundamental to heterogeneous catalysis. However, parameters such as surface area and pore size are often of great importance in determining the behaviour of a catalyst. It is essential to provide a large contact between the reactants and the surface of the solid.

Solid acids and bases are extensively used in catalysis , and Lewis acid / Lewis base definitions are convenient for a clear description of solid acid and base catalysis. Thus a metal fluoride , which is ionic, behaves as a base and a fluoride ion donor, while a covalent metal fluoride acid is a fluoride ion acceptor.

1. 1 Acid Base Concepts

The concept of what constitutes an acid or base has developed as chemical theory has evolved. In one of the earliest studies, Lavoisier suggested that all acids contain oxygen[2], which is responsible for the

acidity characteristic. In 1810, Davy suggested that the essential constituent was not oxygen but hydrogen[3,4]. Later on Leibig stated that acids were substances which contained hydrogen replaceable by metal[5]. Based on the hydrogen concept, and the ionic chemical theory, Arrhenius introduced another definition[6], in which an acid is regarded as a compound containing hydrogen which when dissociated in water yielded hydrogen ions.

$$H_xB \rightleftharpoons xH^+ + B^{x-} \qquad \text{Eq. 1.1}$$

A base is regarded as a compound which furnished hydroxyl ions in aqueous solution

$$M(OH)_y \rightleftharpoons M^{+y} + yOH^- \qquad \text{Eq. 1.2}$$

According to this definition , neutralisation is the reaction of hydrogen ion H^+ generated by the acid, with the hydroxyl, OH^-, generated by the base to give water.

$$H^+ + OH^- \rightleftharpoons H_2O \qquad \text{Eq. 1.3}$$

The Arrhenius interpretation of an acid and base was a subject of many objections, such as, the concept is restricted to aqueous solution, therefore it cannot be applied to solution in other solvents. The concept is incompatible with thermodynamic studies which suggested that the existence

of free protons in aqueous solution is improbable[7]. The hydration energy of the hydrogen ion has been calculated as 256 k cal mol^{-1}. Thus it is to be expected that , this ion can exist only in the hydrated form, usually presented in its simplest form by H_3O^+. As results of these objections other definitions were introduced.

Bronsted–Lowry Definion

This concept of acids and bases was developed independently by J. N. Brønsted and T. M. Lowry in 1923[8,9]. The Brønsted– Lowry definition involve a proton transfer process. According to this definition an acid is defined as a species that acts as a proton donor, and a base is a species that acts as proton acceptor. In term of this approach, acids and bases are characterised and intercalibrated by the equation 1.4.

$$\underset{\text{Acid}}{A} \rightleftharpoons \underset{\text{Base}}{B} + \underset{\text{Proton}}{H^+} \qquad \text{Eq. 1.4}$$

On losing a proton acid A becomes a base B. The base will then tend to regain the proton and revert to the acid A. Acid and base are said to be conjugate with one another and related by the proton transfer represented by the equation 1.5.

$$\underset{\text{Acid}_1\ \text{Base}_1}{HB + H_2O} \rightleftharpoons \underset{\text{Acid}_2\ \text{Base}_2}{H_3O^+ + B^-} \qquad \text{Eq. 1.5}$$

where $base_1$ and $base_2$ are the conjugated bases of $acid_1$ and $acid_2$ respectively. The equilibrium is towards the weaker acid and base. The Brønsted–Lowry definition suffered from the limitation to hydrogen containing compounds.

Solvent System Definition:

In terms of the self ionisation of water, the Arrhenius definition may be restated as follows:

An acid is a solute that increases the concentration of the characteristic solvent cation H_3O^+ for water by giving this cation as one of the products of its ionic dissociation in solution. A base is a solute that increases the characteristic solvent anion concentration OH^- for water by giving this anion as one of the products of its ionic dissociation in solution. These definitions can be extended to other solvents for which a self ionisation process is feasible. The first such extension appears to have been made by Franklin for the liquid ammonia system[10].

$$2\ NH_3 \rightleftharpoons NH_4^+ + NH_2^- \qquad \text{Eq. 1.6}$$

The solvent system definition is unsatisfactory because acid base phenomena are not restricted to self ionising solvents.

1.1.1 Lewis Acid Base Definition

In an attempt to overcome some of the limitations of the previous definitions, an electronic theory was proposed by G. N. Lewis in 1923[11] and further emphasized in 1938[12].

In 1920, Langmuir, came to the conclusion that, within the context of the proton definitions, bases must act as electron pair donors[13]. The formation of a chemical bond required the presence of a shared electron pair, and the transfered proton had no valence electrons. Therefore, the base must logically be the electron pair source.

Subsequently, Lewis generalized this statement to all species which are capable of assuming the role of electron pair acceptor or donor. He defined a basic substance as one which has a lone pair of electrons which may be used to complete the stable group of another atom, and an acid substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms. In terms of the molecular orbital theory the Lewis definition can be expressed as follows:

A base is a species that employs a doubly occupied orbital in initiating a reaction, and an acid is a species that employs an empty orbital in initiating a reaction. It is clear that this definition can be applied to a heterogenous gas–solid system. However, a Lewis acid site on a solid surface can be considered as a site which has an unoccupied orbital, with a high affinity for an electron pair, so that a major decrease in free energy is obtained when such a site shares an electron pair donated by an

adsorbed base molecule. Lewis base sites on the surface are those which have electron pairs available at a high energy level, and a major decrease in free energy is obtained if they share this electron pair with an adsorbed electron pair acceptor. The acid– base reaction is shown as an equilibrium process in equation 1.7.

$$A + B \rightleftharpoons A : B \qquad \text{Eq. } 1.7$$

It is clear that the Lewis definition is more general than the others described. For example within the protonic concept, the molecule or ion does not accept a proton unless an unshared electron pair is available on the substance that acts as base.

$$H^+ + : \underset{H}{\overset{H}{N}} : H \rightleftharpoons \left[H : \underset{H}{\overset{H}{N}} : H \right]^+ \qquad \text{Eq. } 1.8$$

Although the Lewis definition is widely used in acid base chemistry and it has overcome the limitations of the previous definitions, it has been the subject of some objections. Most importantly there is no uniform scale of acid and base strength, instead, acid– base strength are variable and dependent upon the reaction chosen.

The ability of a strong acid or base to displace a weaker one from its compound as proposed by Lewis, gives rise to the question of an acid– base strength order. Accordingly the study of a large number of displacement reactions of the type shown in equation 1.9 should allow an

ordering of the strength of acids towards a particular base.

$$\underset{\text{Acid}}{A} + B : \overset{\backsim}{A} \longrightarrow B : A + \underset{\text{Acid}}{\overset{\backsim}{A}} \qquad \text{Eq. 1.9}$$

A further complication occurs in the assumption that the order of the acid strength is independent of the reference base. Within recent years, it has been shown that the order of acid strength is determined by the reference base chosen[14,15]. For example, fluoride ion affinities are commonly used when comparing the acidities of inorganic fluorides in the gas phase[16–18].

Despite its limitations, it would seem that the Lewis acid base definition is the most suitable for describing heterogenous gas solid reaction.

1. 2 The Chemistry of Sulphur Tetrafluoride

Sulphur tetrafluoride is a colourless gas at room temperature. It condenses to a colourless liquid (b. p $-38\,^{\circ}C$) and solidifies at $-121\,^{\circ}C$. Sulphur tetrafluoride is a highly hygroscopic material. It hydrolyses rapidly and exothermically in aqueous media leading to the formation of HF according to the following equation[19].

$$SF_4 + H_2O \longrightarrow SOF_2 + 2HF \qquad \text{Eq. 1.10}$$

The subsequent hydrolysis of the thionyl fluoride occurs somewhat less rapidly. It is therefore difficult to handle small quantities of sulphur

tetrafluoride. It must be manipulated in rigorously dry glass apparatus. Stainless steel and Monel metal are all quite inert to sulphur tetrafluoride at ambient temperature[19]. Therefore the use of apparatus constructed from these metals greatly simplifies the handling of sulphur tetrafluoride. Sulphur tetrafluoride has been found to be of the same order of toxicity as phosgene $COCl_2$[20], and the ease with which it hydrolyses makes extreme care necessary when working with this fluoride.

The structure of sulphur tetrafluoride has been established by study of its vibrational spectrum[21], N.M.R spectrum[22], and microwave spectrum[23]. The vibrational spectra suggested that the structure had symmetry C_{2v}. This led to the proposal that the stucture was that of a trigonal bi-pyramid, in which one of the three equatorial atoms was replaced by a lone pair of electrons. This has been confirmed by nuclear magnetic resonance studies which showed that sulphur tetrafluoride has two inequivalent sets of fluorine atoms. The microwave spectrum, however, showed that marked deviation occured from trigonal bi-pyramid. As a result of these studies, the structure of sulphur tetrafluoride was suggested to be a distorted trigonal bi-pyramidal structure, in which two fluorine atoms and an unshared electron pair are in the equatorial position, and the other fluorine atoms are in the axial position as shown in figure 1.1. Bond distances and angles are as follows:

$$dSF_1 = dSF_2 = 1.64 \pm 0.003 \text{ Å}$$

$$dSF_3 = dSF_4 = 1.455 \pm 0.003 \text{ Å}$$

$$\widehat{F_2SF_1} = 186.56°$$

$\hat{F_4}SF_3 = 101.33°$

Sulphur tetrafluoride is widely used in both inorganic and organic chemistry. It reacts with Lewis acid fluorides forming adducts containing the SF_3^+ cation according to the following equation[24,25].

$$SF_4 + AF_n \longrightarrow SF_3^+AF^-_{n+1} \qquad \text{Eq. 1.11}$$

A typical example of this type of reaction is the reaction of sulphur tetrafluoride with boron trifluoride according to the following equation.

$$SF_4 + BF_3 \longrightarrow SF_3^+BF_4^- \qquad \text{Eq. 1.12}$$

The SF_3^+ exhibits C_{3v} symmetry as shown in figure 1.2. The crystal structure of trifluorosulphur tetrafluoroborate, $SF_3^+BF_4^-$, has been determined from three dimensional X-ray data[25]. The atomic arrangement is illustrated in figure 1.3.

Sulphur tetrafluoride can also act as a weak Lewis acid, that is an electron pair acceptor, forming an adduct containing the SF_5^- anion[26,27] according to the equation 1.13.

$$SF_4 + MF \longrightarrow M^+SF_5^- \qquad \text{Eq. 1.13}$$

An example is the reaction of sulphur tetrafluoride with caesium fluoride according to the equation 1.14.

Figure 1.1

The structure of SF_4

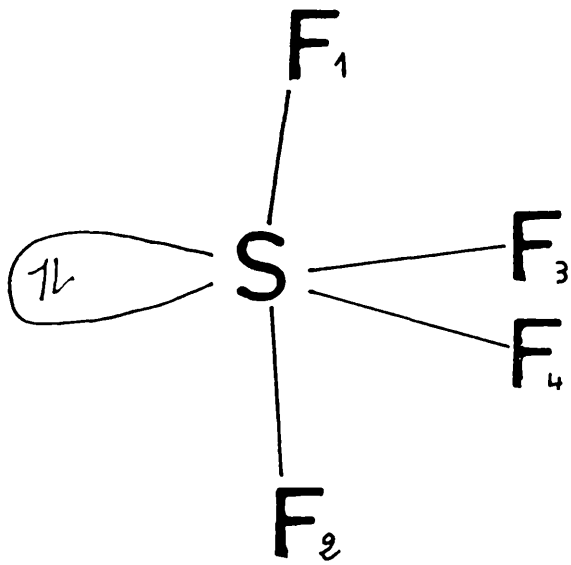


Figure 1.2

The Structure of SF_3^+

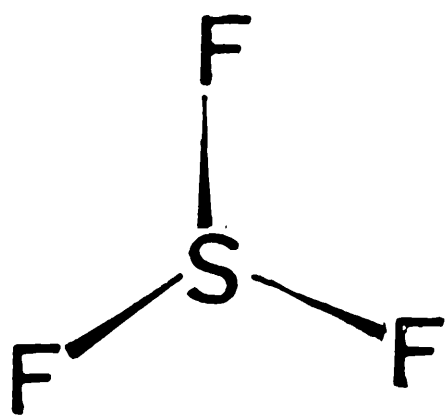
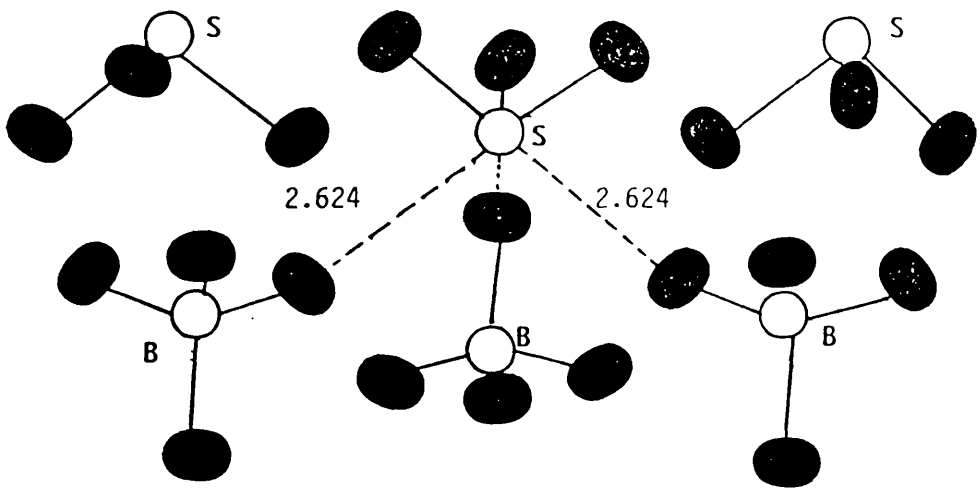


Figure 1.3

The strucure of $SF_3^+BF_4^-$



$$CsF + SF_4 \longrightarrow Cs^+SF_5^- \qquad \text{Eq. 1.14}$$

The structure of the anion has been characterised spectrospically as being square pyramidal[28,29], as shown in figure 1.4.

In organic chemistry sulphur tetrafluoride is widely used as a fluorinating agent. It has been found to be a remarkably effective reagent for the selective replacement of carbonyl compounds[30] ,equation 1.15.

$$\text{>C=O} + SF_4 \longrightarrow \text{>}CF_2 + SOF_2 \qquad \text{Eq. 1.15}$$

Typical examples for the above type of reaction are given in the following equations:

$$CH_3CHO + SF_4 \xrightarrow{50\,^\circ C} CH_3CHF_2 + SOF_2 \qquad \text{Eq. 1.16}$$

$$CH_3COCH_3 + SF_4 \xrightarrow{110\,^\circ C} CH_3CF_2CH_3 + SOF_2 \qquad \text{Eq. 1.17}$$

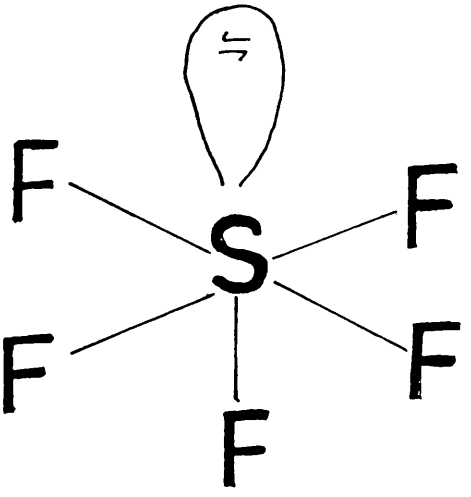
Organoiminosulphur(IV) difluoride compounds, $R–N=SF_2$, have also been obtained by the reaction of sulphur tetrafluoride with organic compounds having carbon – nitrogen multiple bond[31] as illustrated in the following examples.

$$R–N=C=O + SF_4 \xrightarrow{350\,^\circ C} RN=SF_2 + COF_2 \qquad \text{Eq. 1.18}$$

$$R–C\equiv N + SF_4 \xrightarrow{350\,^\circ C} RCF_2N=SF_2 \qquad \text{Eq. 1.19}$$

Figure 1.4

The structure of SF_5^-



Replacement of halogen atom by fluorine in organic compounds can be also achieved by means of sulphur tetrafluoride[32], equation 1.20.

$$CCl_4 + SF_4 \xrightarrow{225-325\ ^{\circ}C} CCl_3F + CCl_2F_2 + CClF_3 + SCl_2 \qquad \text{Eq. 1.20}$$

It is clear from these examples that sulphur tetrafluoride undergoes a wide range of chemical reactions, and exhibits both Lewis acid and base behaviour. In addition, the availability of ^{18}F and ^{35}S radiotracers, makes it a very useful probe substance for the study of Lewis acid–base reactions.

1.3 Chlorine Monofluoride

Chlorine monofluoride is a colourless gas and solid (m.p -155 C°). The liquid (b.p -101.5 C°) has a yellow cast. Unlike the monofluorides of iodine and bromine, chlorine monofluoride is thermally stable at room temperature[33]. It is a vigorous oxidizer, immediately and explosively hydrolysed by water.

Assuming that chlorine monofluoride is strictly covalent, the bond distance deduced from the parent halogens is 1.712 A [34]. The experimental bond distance determined by electron diffraction measurement is 1.63 A[35]. This agrees well with the value of 1.6281 A determined by microwave spectroscopy[36], that is 5% shorter than the calculated bond distance. On this basis it has been suggested that chlorine monofluoride possesses some ionic character. It would be expected that the fluorine atom on account of its high electronegativity would be the more negative partner

in the molecule, therfore the direction of the polarisation in the molecule is $Cl^{\delta+} - F^{\delta-}$.

Chlorine monofluoride is a powerful fluorinating agent and will react with many metals either at elevated temperatures or at room temperature, converting them to the appropriate fluoride[37]. Chlorine monofluoride reacts also with alkali metal fluorides to form relatively stable salts of the type $M^+ ClF_2^-$ [38]. Since only one infrared active band is observed for ClF_2^-, the difluorochlorate anion, ClF_2^-, appears to have a linear structure[39]. Similar Lewis acid behaviour of chlorine monofluoride has been found when it reacts with nitrosyl fluoride at low temperature[39], equation 1.21.

$$NOF + ClF \longrightarrow NO^+ClF_2^- \qquad \text{Eq. 1.21}$$

However the solid formed is only stable at low temperature.

The addition of the molecule to multiple bonds such as C=C, C=O, C=S, S=N and C=N represents the most common use of chlorine monofluoride[40]. Some of these reactions, require a catalyst. However, the perhaloalkyl hypochlorites are easly prepared by the metal fluoride catalysed reaction of perhaloalkyl carbonyl compounds[41].

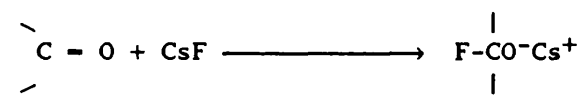
$$\begin{array}{l} R_f' \\ \diagdown \\ \quad CO \\ \diagup \\ R_f \end{array} + ClF \xrightarrow[-20\ ^\circ C]{CsF} \begin{array}{l} R_f' \\ \diagdown \\ F\text{–}C\text{–}O\text{–}Cl \\ \diagup \\ R_f \end{array} \qquad \text{Eq. 1.22}$$

$R_f = R_f' = F$

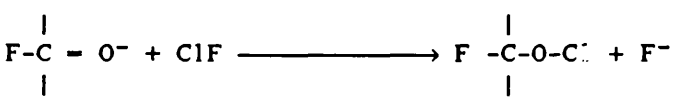
$R_f = R_f' = CF_3$

$R_f = F,\ R_f' = CF_3$

These may be regarded as a base catalysed oxidative addition to the carbonyl group, where the first step is attack by the base (fluoride ion) on the electrophilic carbon of the carbonyl group to form fluoroalkoxide intermediate, the latter is in turn oxidised by chlorine monofluoride to form the hypochlorite and generate fluoride. This is illustrated in the following sequence:



Eq. 1.23



Eq. 1.24

It was found that the formation of perhaloalkyl hypochlorites by the addition of chlorine monofluoride to substrate carbonyl groups is also catalysed by strong Lewis acids such as HF, BF_3, AsF_5[42].

$$F_2CO + ClF \xrightarrow[-20\ ^{\circ}C]{HF} CF_3\ COCl \qquad \text{Eq. 1.25}$$

The role of the Lewis acid in catalysis of hypochlorite formation involves a polarising interaction of the Lewis acid with chlorine monofluoride in a manner that enhances the positive character of the chlorine. This is illustrated for hydrogen fluoride by the equation.

$$Cl^{\delta+} - F^{\delta-} + HF \longrightarrow Cl^{\delta\delta+} \,..\, F^{\delta-} \,..\, H \,..\, F^{\delta-} \qquad \text{Eq. 1.26}$$

Chlorofluorination has also been used to prepare the difunctional decafluoropentane dihypochlorite, equation 1.27 as well as pentafluorosulphur hypochlorite, equation 1.28 [41].

$$F-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-F + 2\ ClF \xrightarrow[-20\ ^{\circ}C]{CsF} Cl-O-(CF_2)_5-O-Cl \qquad \text{Eq. 1.27}$$

$$F_4SO + ClF \xrightarrow[-20\ ^{\circ}C]{CsF} SF_5OCl \qquad \text{Eq. 1.28}$$

The addition of chlorine monofluoride to the other bonds does not require a catalyst in most cases[40].

A typical example of chlorofluorination with chlorine monofluoride will be discussed in a later section.

1.4 Sulphur Chloride Pentafluoride

Sulphur chloride pentafluoride is colourless gas at room temperature. It condenses to a colourless liquid at $-19\ ^{\circ}C$ and freezes to a colourless solid at $-64\ ^{\circ}C$. Thermally, sulphur chloride pentafluoride is stable up to 400C°[19]. The ability of SF_5Cl to give SF_5 radical is an important feature of its chemistry[43–45].

$$SF_5Cl \xrightarrow[uv]{h\nu} SF_5\cdot + Cl\cdot \qquad \text{Eq. 1.29}$$

It is stable towards dilute acids but it is rapidly hydrolyzed by dilute alkali[46] according to the following equation.

$$SF_5Cl + 8KOH \longrightarrow 5KF + KCl + K_2SO_4 + 4H_2O \qquad \text{Eq. 1.30}$$

Sulphur chloride pentafluoride can be added by free radical mechanism to the carbon–carbon double bond in certain olefins, such as ethene, as well as chloroolefins and fluoroolefins[45], such as vinyl chloride and fluoroethylene

Addition of SF_5Cl to the C = O function is much less effective[47] than for $\overset{\diagup}{\underset{\diagdown}{C}} = \underset{\diagup}{\overset{\diagdown}{C}}$

1.5 Mercury(II) Fluoride

Mercury(II) fluoride is a colourless solid when pure which is extremely sensitive to moisture. The presence of a limited amount of moisture causes a rapid yellowish discolouration of the surface possibly due to the formation of $HgF_2.2H_2O$[48]. This colour changes to orange pink with further exposure, due to the formation of a layer of mercury(II) oxide. mercury(II) fluoride must therefore be handled carefully, due to its high sensitivity to moisture. It must be stored and manipulated in a rigorously dry atmosphere. It decomposes at its melting point at about 645 °C .

In mercury halides, mercury(II) fluoride is the only simple ionic compound[49], it crystallises in the cubic fluorite structure[50] as shown in

figure 1.5. The cation Hg^{++} is surounded by 8 fluorine anions F^- in a cubic arrangement, and the anion F^- is surrounded by 4 mercury cations Hg^{++} situated at the corners of a tetrahedron. The bond distance between the cation and the anion in this structure is 2.40 Å (50).

Geometrical considerations indicated that the adoption of the fluorite structure of AX_2 type compounds occurs when the radius ratio $r_+ : r_-$ is greater than 0.73(51). The influence of the radius ratio is illustrated in group(II). For magnesium and zinc the ionic radii are 0.65 and 0.74 Å respectively. These compounds form fluoride with the rutile structure, figure 1.6. Calcium (ionic radius 0.99 Å), strontium (1.13 Å), barium (1.35 Å), cadmium (0.97 Å) and mercuric (1.10 Å) fluorides have the fluorite structure(52).

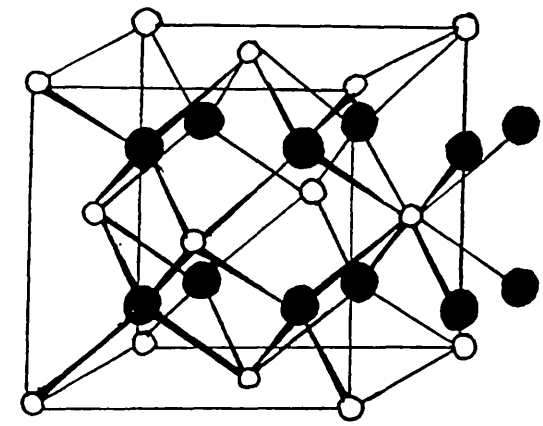
Alkali metal fluorides crystallise with the rock salt structure(53), in which each ion is surrounded octahedrally by six ions, figure 1.7. The bond distances of this series of fluorides are(54)

Li—F,	Na—F,	K—F,	Rb—F,	Cs—F
2.07	2.13	2.69	2.84	3.04 Å

The ionic radii of the cations are

Li+	Na+	K+	Rb+	Cs^+
0.74	1.04	1.33	1.48	1.69 Å

Mercury(II) fluoride is quite widely used as a fluorinating agent for organic



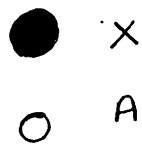
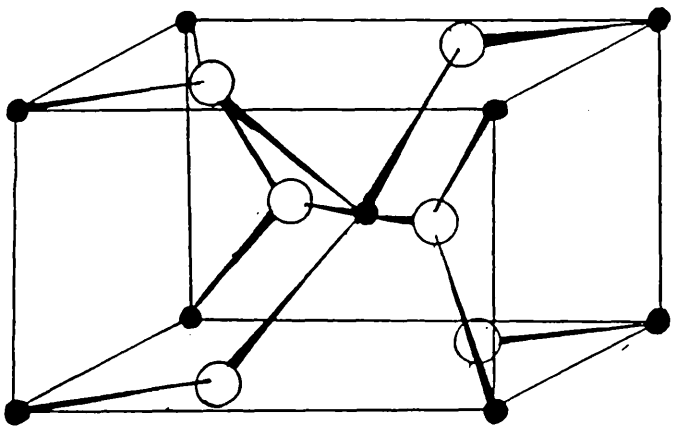


Figure 1.5

The fluorite structure for AX_2 type compounds

Figure 1.6

The rutile structure for AX_2 type compounds

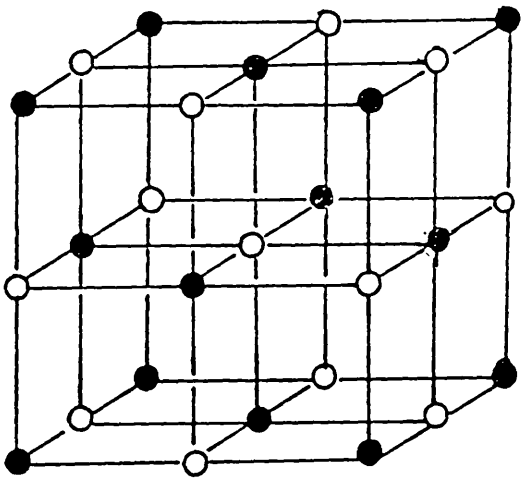


● A

○ X

Figure 1.7

The unit cell of CsF



● F

○ M = Cs

compounds, and when heated with metals such as copper, lead, tin, magnesium, and chromium converts them to the corresponding fluoride[51]. It is a very potent fluorinating reagent for the replacement of halogen by fluorine and reacts with aliphatic bromides very violently[55], equation 1.31.

$$C_2H_5Br \xrightarrow[0\,^{\circ}C]{HgF_2} C_2H_5F \qquad \text{Eq. 1.31}$$

In polybromoderivatives, two and even three bromine atoms attached to the same carbon atom can be replaced by fluorine using *m*ercury(II) fluoride[56]. Typical examples are given in the following equations:

$$CHBr_2\text{-}CHBr_2 \xrightarrow[150\,^{\circ}C]{HgF_2} CHF_2CHBr_2 \qquad \text{Eq. 1.32}$$

$$CHBr_3 \xrightarrow[RT]{HgF_2} CHF_3 \qquad \text{Eq. 1.33}$$

Iododerivatives react with HgF_2 so vigorously that their dilution with chloroform or methylene chloride is advisable[55], equation 1.34.

$$CHI_3 \xrightarrow[RT]{HgF_2} CHF_3 \qquad \text{Eq. 1.34}$$

Polychloroderivatives are less reactive[55,56]. Usually only two halogen atoms are replaced, equation 1.35.

$$CHCl_3 \xrightarrow{HgF_2} CHClF_2 \qquad \text{Eq. 1.35}$$

The reaction between HgF_2 and fluoroolefins has been also reported to be a route to polyfluoro–alkyl derivatives of mercury[57], equation 1.36.

$$CF_2 = CFCl \xrightarrow[100\,^{\circ}C]{HgF_2} CF_3.CFCl.HgF \qquad \text{Eq. 1.36}$$

The addition of fluorine across carbon–nitrogen bond in unsaturated systems has been achieved with HgF_2[58]. For example *m*ercury(II) fluoride is quite effective in adding fluorine across the carbon–nitrogen double bond of perfluoro–2–azopropene $CF_3N = CF_2$. The activity of the reagent, in comparison with other metal fluorides, follows the order, $AgF_2 > AgF > HgF_2 > CoF_3 > PbF_4 > MnF_3$. Both cyanogen and cyanogen chloride react with HgF_2 to give, at 240 C° a mixture of $CF_3-N=CF_2$ and mercurial bistrifluoromethyl amide $Hg[N(CF_3)_2]_2$. The latter is known to be formed from HgF_2 and $CF_3-N = CF_2$.

Mercury(II) fluoride has been found to be a substitute for the addition of polar fluorides such as ClF to sulphur–nitrogen triple bond of NSF_3 to form pentafluorosulphanyl amine F_5S-NCl_2 [59]. Although, ClF does not attack SN triple bonds, in the presence of HgF_2, the addition of ClF can be achieved in a quantitative yield.

$$N \equiv SF_3 + 2\ ClF \xrightarrow{HgF_2} F_5S{-}NCl_2 \qquad \text{Eq. 1.37}$$

Alkali metal fluorides are also used as reagents for introducing fluorine. However, potassium fluoride is the most frequently used for halogen exchange. The other alkali metal fluorides are either less efficient or less available. The efficiency of alkali metal fluorides with respect to the

replacement reactions falls in the sequence[60,61].

CsF >RbF >KF >NaF >LiF

The ease of replacement by fluorine increases in the sequence Cl < Br < I, and from primary to tertiary halogen.

In unsaturated fluorocarbon systems, fluoride ion as a nucleophile occupies a unique position, analogous to that of the proton as an electrophile in unsaturated hydrocarbons[62,63]. Fluoro-olefins with CF_2^- groups are especially reactive towards fluoride ions and this high reactivity apparently extends to some hetero-atom organic compounds[64] such as $CF_2{=}O$. Unsaturated fluorocarbon systems containing nitrogen of the type $CF_2{=}N$ exhibit a high degree of reactivity towards fluoride ions[65-67]. For example fluoride ion catalyzed reactions with fluorocarbons nitriles, which may involve an intermediate perfluoro alkanamine ion. The ionic fluorides, CSF,KF and HgF_2 readily attack $CF_2 = NF$ to form an intermediate perfluoromethanamine ion CF_3NF^- according to the equation 1.38[68].

$$MF + CF_2 = NF \longrightarrow M^+FNCF_3^- \qquad \text{Eq. 1.38}$$

The CF_3NF^- anion formed in the initial step functions as a reactive nucleophile in competition with the excess fluoride. The subsequent reaction of the anion CF_3NF^- with $CF_2 = NF$ yields perfluro-N-methyl formamidine, equation 1.39.

$$CF_3\text{–}NF^- + CF_2{=}NF \xrightarrow[-F^-]{MF} CF_3\text{–}NF\text{–}CF{=}NF \qquad \text{Eq. 1.39}$$

The formamidine is also obtained with HgF_2 but in lower yield[67]. In the case of HgF_2 and in contrast to KF, a considerable amount of $CF_2 = NF$ is absorbed by HgF_2.

1.6 The Chlorofluororination of Sulphur Tetrafluoride

Sulphur chloride pentafluoride was first isolated and characterised as a minor constituent in the product of the reaction of fluorine with sulphur dichloride[69]. Many preparative methods have been developed subsequently, amongst them are the chlorofluorination of sulphur tetrafluoride with chlorine monofluoride. A high temperature is required for this reaction[70]. However, in the presence of caesium fluoride this reaction occurs rapidly at ambient temperature with a high yield and minimum by–product formation[71], equation 1.40.

$$SF_4 + ClF \xrightarrow[RT]{CsF} SF_5Cl \qquad \text{Eq. 1.40}$$

It has been found that SF_5Cl can be obtained by the chlorofluorination of SF_4 according to the equation 1.41 [27] .

$$SF_4 + Cl_2 + CsF \longrightarrow SF_5Cl + CsCl \qquad \text{Eq. 1.41}$$

The above reaction was reported to proceed via the formation of $CsSF_5$, which resulted from the reaction of SF_4 and CsF. The chlorine subsequently

converts this salt to SF_5Cl and CsCl. The role of the metal fluoride in the equation 1.40 is not clearly understood. There have been a number of attempts to describe the mechanism by which the reaction proceeds. Shack and coworkers[71] suggested that the catalytic effect of caesium fluoride in this reaction is probably due to the polarisation of sulphur tetrafluoride, which makes it readily susceptible to oxidation by chlorine monofluoride. The formation of the salt $Cs^+ SF_5^-$, which has been also reported to be an intermediate in the sulphur chloride pentafluoride synthesis[27], can also occur according to Shack. The anion is then oxidized by chlorine monofluoride to give sulphur chloride pentafluoride. The overall reaction scheme is therefore:

$$CsF_{(s)} + SF_{4(g)} \longrightarrow Cs^+SF_5^-{}_{(s)} \qquad \text{Eq. 1.42}$$

$$Cs^+SF_5^-{}_{(s)} + ClF_{(g)} \longrightarrow CsF_{(s)} + SF_5Cl_{(g)} \qquad \text{Eq. 1.43}$$

This mechanism, involving formation and reaction of the species $Cs^+SF_5^-$, has been shown to be incorrect by Kolta and coworkers[72]. The mechanism does not take into account the reaction between chlorine monofluoride and caesium fluoride. Experiments involving radiochemically labelled $[^{35}S]$-sulphur tetrafluoride and $[^{36}Cl]$ chlorine monofluoride carried out in this Department, led to the conclusion that the formation of sulphurchloride pentafluoride is a true surface reaction involving adsorbed chlorine monofluoride and adsorbed sulphur tetrafluoride. The results obtained have shown that there is an interaction between chlorine monofluoride and caesium fluoride. Furthermore a considerable quantity of the chlorine monofluoride adsorbed is retained by the caesium fluoride surface and does not participate to any appreciable extent in the subsequent reaction with sulphur tetrafluoride. Kolta and coworkers suggested that the

formation of the $Cs^+ ClF_2^-$ species is responsible for the retention observed.

A similar retention of [^{35}S] sulphur tetrafluoride was observed, although the quantity retained was less than that observed for chlorine monofluoride. Furthermore, unlike chlorine monofluoride retention, which led to catalyst poisoning, there was no evidence to suggest that the retained [^{35}S] sulphur tetrafluoride acts as a catalyst poison[72]. As a result of their study, they proposed that the mechanism could be best described by the following equations:

$$SF_{4(g)} + CsF_{(s)} \rightleftharpoons CsF.SF_{4(ads)} \qquad \text{Eq. 1.44}$$

$$CsF.SF_{4(ads)} \longrightarrow Cs^+SF_5^-{}_{(s)} \qquad \text{Eq. 1.45}$$

$$ClF_{(g)} + CsF_{(s)} \rightleftharpoons CsF.ClF_{(ads)} \qquad \text{Eq. 1.46}$$

$$CsF.ClF_{(ads)} \longrightarrow Cs^+ClF_2^-{}_{(s)} \qquad \text{Eq. 1.47}$$

$$CsF.ClF_{(ads)} + CsF.SF_{4(ads)} \longrightarrow SF_5Cl_{(g)} + 2\ CsF_{(s)} \qquad \text{Eq. 1.48}$$

Thus adsorbed chlorine monofluoride and adsorbed sulphur tetrafluoride are the active species in the formation of sulphurchloride pentafluoride rather than $Cs^+ SF_5^-{}_{(s)}$ and $ClF_{(g)}$.

1.7 The Aim of the Present Work

The chlorofluorination of sulphur tetrafluoride in the presence of caesium fluoride indicates that chlorine monofluoride behaves as a catalyst poison[72]. According to Mews and coworkers, chlorine trifluoride reacts with *m*ercury(II) chloride to give *m*ercury(II) fluoride and chlorine monofluoride[73], equation 1.42.

$$HgCl_2 + 2ClF_3 \xrightarrow{25\ C^\circ} HgF_2 + 4ClF \qquad \text{Eq. 1.4}$$

9

This reaction was reported to be straight forward and a yield of 91% was obtained. Thus, no interaction between ClF and HgF_2 was observed, that is no $Hg^+ClF_2^-$ species. Therefore, would mercury(II) fluoride be a better catalyst than caesium fluoride for the above reaction ?

The chlorofluorination of sulphur tetrafluoride with chlorine monofluoride at room temperature to give sulphurchloride pentafluoride was chosen as a model reaction to clarify further the catalytic activity of mercury(II) fluoride. The room temperature reaction involving [^{35}S]– sulphur labelled sulphur tetrafluoride and [^{36}Cl]– chlorine labelled chlorine monofluoride with mercury(II) fluoride pretreated either by hexafluoroacetone or by sulphur tetrafluoride were examined.

CHAPTER TWO

CHAPTER TWO

Experimental

2.1 Equipment

Due to the highly hygroscopic properties of most of the materials used in this work, all experiments were performed in vacuo (10^{-4} Torr). Solids sensitive to moisture were stored in an inert atmosphere box (H_2O < 10 ppm).

2.1.1 The Vacuum Systems

Depending on the properties of the reactants, two different systems were used, a Pyrex glass line for experiments involving radiochemical counting techniques, and a Monel metal line which was used for handling substances reacting with glass.

a) The Pyrex Glass Vacuum Line

The vacuum line was basically an enclosed Pyrex glass structure. The line was evacuated by means of a mercury diffusion pump, together with an oil sealed rotary pump. A series of waste traps cooled in liquid nitrogen was used to protect the pumps from any volatile materials in the line. The pumps and waste traps could be isolated from the rest of the line using either a glass tap or a high vacuum stopcock (Rotaflo). The different

parts of the line were isolated when required by the same means.

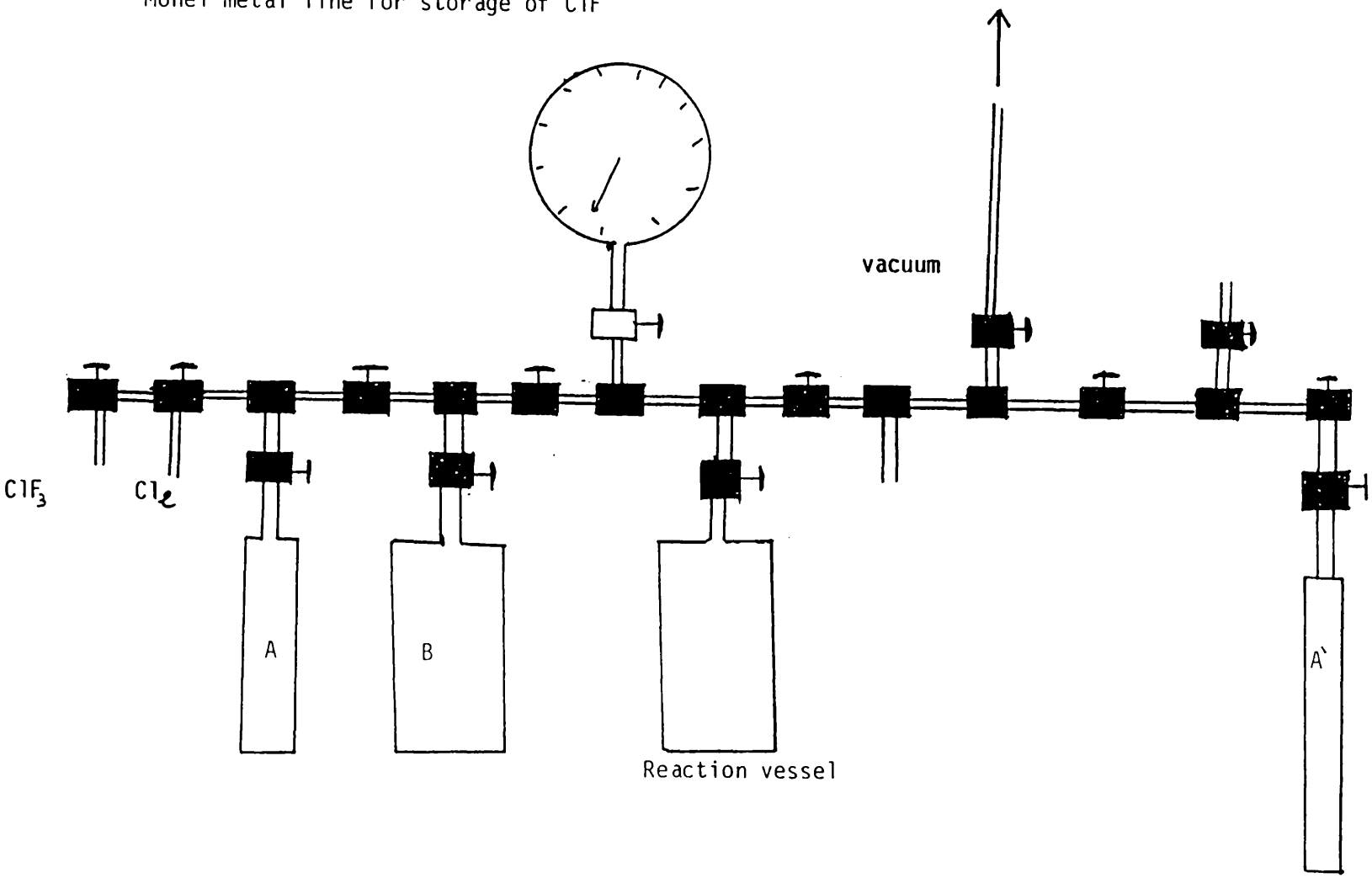
The vacuum line was equipped with a mercury manometer or a Bourdon tube pressure gauge (Heise), to measure precisely the pressures. A vacustat was used to estimate the pressure achieved by the pumps. The main manifold, consisted of several outlets to which a reaction vessel and a secondary manifold which had B14 ground glass sockets attached. Both reaction vessel and the other manifold could be isolated using high vacuum stop cocks (Rotaflo). Evacuable flasks and ampoules, equipped with high vacuum stopcocks and B14 cones, were attached to the sockets of the manifold using Kel−F grease. All glassware was flamed out before use with a gas oxygen flame while the line was pumped to remove as much as possible moisture adsorbed on the surface of the glass.

b) The Monel Metal Line

A Monel metal line was used in this work for the preparation of chlorine monofluoride. It was constructed using 2/5 inch o.d Monel tubing and Monel valves (Autoclave engineer) to enable the different parts of the line to be separated, figure 2.1. The line was equipped with Budenberg Bourdon tube gauge for pressure measurement. A Monel metal reaction vessel and three additional Monel metal vessels, one large (B) and the other smaller ones (A and A') were used as storing vessels and attached to the system by the same means. A Monel metal pressure vessel containing elemental silicon and connected to the line was used as a waste trap. The disposal of chlorine trifluoride was carried out by condensing it in this vessel and allowing the reactants to stay overnight at room temperature.

Figure 2.1

Monel metal line for storage of ClF



The products subsequently were pumped out in a fume cupboard. Cylinders of chlorine trifluoride and chlorine were also connected. The Monel metal section was connected to the Pyrex waste traps and the pump via a 2/5 inch glass metal joint.

2.1.2 Gas Uptake Apparatus

The determination of gas uptake by a solid was performed manometrically using the apparatus shown in figure 2.2. The apparatus consisted of a constant volume manometer and a small manifold which had a B14 ground glass socket to which a small bulb of a known volume, fitted with B14 cone and a Rotaflo stopcock was attatched. The system was calibrated accurately before use by means of the constant volume manometer. The latter is shown in more detail in figure 2.3.

The mercury level was altered by admitting air or vacuum to the reservoir via two way stopcocks so that the mercury level in the right hand limb could be brought to a reference mark as required. Changes in pressure were measured using a cathetometer.

2.1.3 The Inert Atmosphere Box

A nitrogen atmosphere Lintott box (H_2O < 10 ppm) was used when handling and storing all moisture sensitive solid samples. Glass vessels were pumped and flamed out before being transferred to the box. The box contained a balance which enabled solid samples to be weighed in a dry atmosphere.

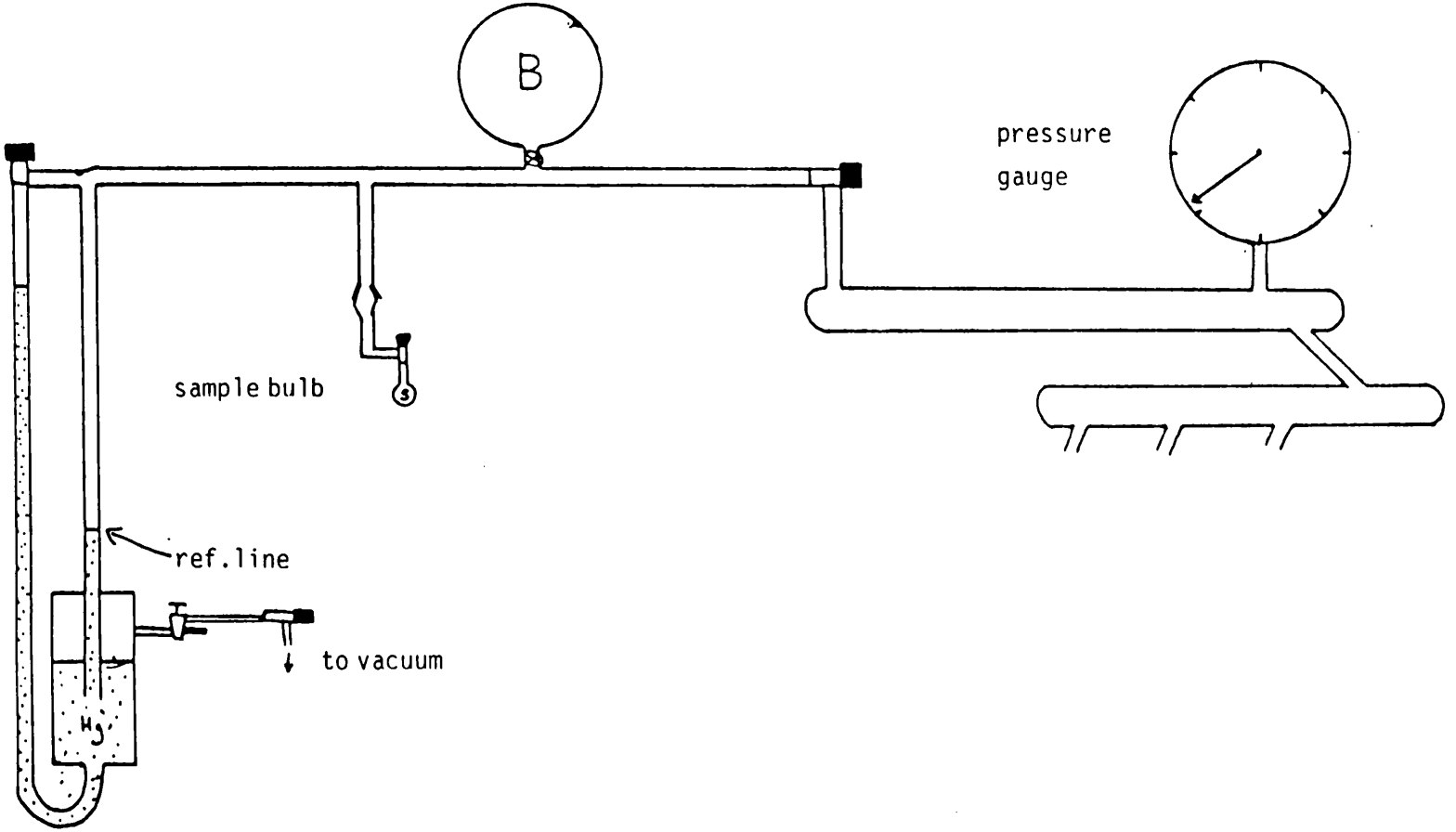


Figure 2.2

Constant volume apparatus

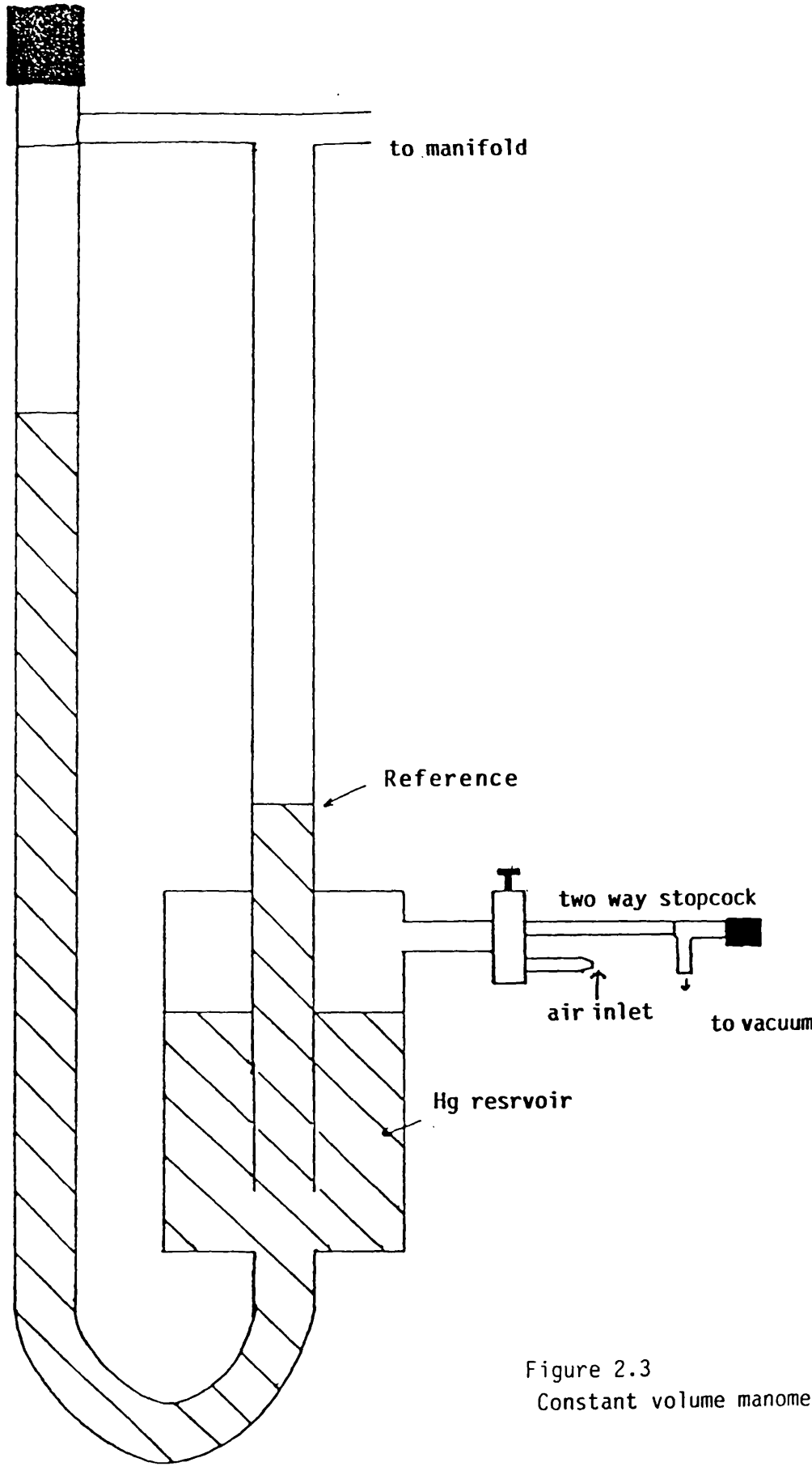


Figure 2.3
Constant volume manometer

2.1.4 Infrared Spectroscopy

Infrared spectroscopic analyses were carried out using a Perkin Elmer 983 grating infrared spectrometer with data station. Spectra of solid samples were obtained as Nujol mulls between AgCl plates. All mulls were prepared in the inert atmosphere box. A Pyrex gas cell of 8 cm path length was used for the gas samples. The cell was fitted with AgCl windows and a B14 cone to enable the cell to be attached to the line. It was also equipped with a J.Young stopcock so that a desired pressure of gas could be isolated in the cell.

2.2 Preparation and Purification of Reagents

2.2.1 Purification of acetonitrile

Acetonitrile is widely used as a solvent in inorganic chemistry. Some Lewis acid fluorides react with impure acetonitrile[74], therefore acetonitrile must be purified before use. The purification method developed in this Department[74] is an extension of that used by Walter and Ramelay[75]. It consisted of multiple reflux of HPLC grade acetonitrile in a Pyrex still equipped with a 0.75 m vacuum jacketed separating column, which was protected from atmospheric moisture. The following steps were used, in each step the solvent was topped and tailed by approximately 3%, quantities being given in parentheses.

I– Refluxed over anhydrous $AlCl_3$ (15 g/l of MeCN) for one hour

followed by rapid distillation.

II– Refluxed over $KMnO_4$ + $LiCO_3$ (both 10 g/l of MeCN) for 15 minutes. At this stage anti–bumping stones were added.

III– Refluxed over $KHSO_4$ (15 g/l of MeCN) for one hour followed by rapid distillation.

IV– Refluxed over CaH_2 (20 g/l of MeCN) for one hour followed by rapid distillation.

V– Refluxed two times over separate portions of CaH_2 (1g/l of MeCN) for one hour in each case followed by rapid distillation.

The acetonitrile was then transferred without exposure to atmospheric moisture into a vessel containing 3A activated molecular sieves, which had been previously heated under vacuum at 190 C° for 24 h. Before being used the acetonitrile was degassed and allowed to stand over the molecular sieves for 24 h and distilled under vacuum onto fresh molecular sieves. The purified acetonitrile has an absorbance at 200 nm[74] of < 0.5 (H_2O reference) and an apparent U.V cut off point Ca. 175 nm. If the acetonitrile was not pure enough, traces of impurities remaining were removed by treatment with activated alumina (neutral, 60 mesh) in vacuo prior to the final molecular sieves treatment.

2.2.2 Purification of Di–ethyl Ether

In order to purify di–ethyl ether, freshly cut sodium metal was added in small pieces to Analar solvent and allowed to stand for 24 hours under atmospheric pressure. To ensure that the di–ethyl ether was dry enough fresh pieces of sodium were added until no further evolution of

dihydrogen was observed. The di-ethyl ether was then degassed and vacuum distilled on to 3A molecular sieves. Finally the di-ethyl ether was allowed to stand over 3A molecular sieves for 48 hours before use.

2.2.3 Preparation and Purification of Chlorine Monofluoride

Chlorine monofluoride can be prepared by several methods[73,76-77]. The one used in this work involved the reaction between chlorine and chlorine trifluoride according to the equation 2.1[77].

$$ClF_3 + Cl_2 \xrightarrow{155\,^{\circ}C} 3\,ClF \qquad \text{Eq. 2.1}$$

The Monel metal line used for the preparation was described previously. The system was passivated with chlorine trifluoride at 200 Torr before use. The procedure for the preparation was as follows.

A measured amount of chlorine trifluoride (10.0 mmol) was admitted into the line and condensed into the vessel A. The same amount of chlorine (10.0 mmol) was condensed in the same vessel. The mixture was allowed to warm to room temperature and then expanded into the line. The exact pressure of the mixture was measured and the valve of the reaction vessel was then closed. The mixture remaining in the line was then condensed into the waste trap. The temperature of the reaction vessel was raised gradually up to 155 °C and left at this temperature for 18 hours. The contents of the reaction vessel were transferred into vessel A.

The separation of chlorine monofluoride from unreacted material and

impurities was performed by low trap–to–trap distillation. Impurities were trapped in the −130 °C bath (liquid N_2/isopentane), the chlorine monofluoride which is volatile at this temperature was condensed into vessel B cooled to −196 °C (liquid N_2). The purity of chlorine monofluoride was determined by means of vapour pressure measurements[78]. Typical data obtained are shown in table 2.1.

2.2.4 Preparation and Purification of Carbonyl Fluoride

Carbonyl fluoride was prepared by the reaction of carbonyl chloride with sodium fluoride in acetonitrile[79]. Purified acetonitrile (15.0 ml) was vacuum distilled into a stainless steel pressure vessel (90 ml) containing sodium fluoride (8.4 g, 20.0 mmol). Subsequently $COCl_2$ (18.0 mmol) was then condensed into the same vessel. The mixture was allowed to react at room temperature for 48 hours.

The carbonyl fluoride so prepared was purified by trap–to–trap distillation at −80 °C (dichloromethane/solid CO_2) and identified by its infrared spectrum ,table 2.2.

2.2.5 Preparation and Purification of Boron Trifluoride[80]

A mixture of concentrated aqueous hydrogen chloride (35.4 w/w%, 16 ml) and 4–chloroaniline (16.0 g, 40.0 mmol) was diazotized at 0 °C with a solution of sodium nitrite (2.9 g, 42.0 mmol) in water (4.3 ml). The 4–chloroaniline was well ground before use. The mixture was stirred magnetically for 30 minutes at the same temperature. A solution of sodium

Table 2.1

Vapour pressure data for ClF

Temprture ^{0}C	Vapour pressure Torr	
	This work	Literature[78]
-139.0	9	10
-128.8	41	40
-120.8	102	100
-107.0	405	400
-100.0	762	760

Table 2.2

Infrared spectrum of COF_2 cm^{-1}

This work	Literature[81]	Assignment
585 (w)	584	ν (A_1)
625 (w)	626	ν (B_2)
774 (m)	774	ν (B_1)
964 (m)	965	ν (A_1)
1245 (s)	1249	ν (B_2)
1930 (s)	1928	ν (A_1)

tetrafluoroborate (7.7 g, 20.0 mmol) in water (9 ml) was added slowly to the mixture and stiring was continued at 0 °C for a further 30 minutes.

The precipitate formed of 4– chlorophenyldiazonium tetrafluoroborate was separated using a Büchner funnel and water pump. The precipitate collected was washed with ethanol and di– ethyl ether and transferred to a vessel, equipped with a B14 cone to enable the vessel to be attached to the vacuum line and a Rotaflo stopcock so that the material inside the vessel could be isolated. The precipate was dried by evacuation at room temperature for 18 hours to ensure that no volatile material was left.

The vessel containing the precipitate was then connected to the Pyrex glass system shown in figure 2.4 in which the thermal decomposition of 4– chlorophenyldiazonium tetrafluoroborate was carried out. Trap A was cooled to – 80 °C (dichloromethane/solid CO_2). Trap B was cooled to a – 196 °C (liquid N_2). The system was connected to the vacuum line via trap B. The vessel containing 4– chlorophenyldiazonium tetrafluoroborate was heated gently with a gas torch until the pressure of the gas released reached 200 Torr. The torch was removed and the system was reevacuated. This sequence was repeated until no further release of gas was observed. Once the decomposition has finished, the stopcock 1 was closed and the boron trifluoride trapped in vessel B was expanded to the line to measure its pressure. It was then condensed over sodium fluoride in stainless steel pressure vessel (90 ml) until required. The infrared spectrum of the boron trifluoride was obtained and typical data are shown in table 2.3.

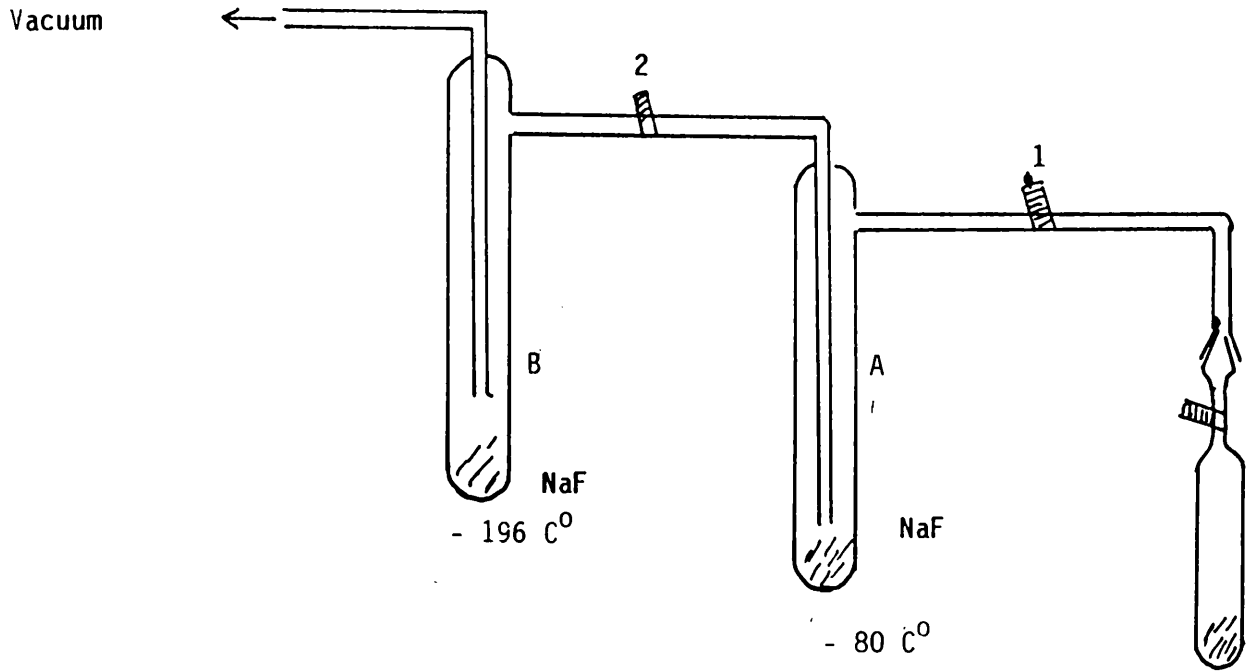


Figure 2.4

Preparation apparatus of boron trifluoride

2.2.6 Purification of Iodine Pentafluoride

The iodine pentafluoride was purified by trap–to–trap distillation over preheated sodium fluoride in order to remove hydrogen fluoride. The iodine pentafluoride was then transferred by vacuum distillation to a vessel containing a dry mercury metal. The mixture was shaken mechanically for 5 minutes at room temperature to remove iodine. Once the mercury metal treatement was finished, iodine pentafluoride was stored over sodium fluoride in a sealed Pyrex glass vessel cooled to $-196\ ^{\circ}C$. The purified iodine pentafluoride was colourless.

2.2.7 Preparation and Purification of Sulphur Tetrafluoride

Although, sulphur tetrafluoride can be prepared by several methods[82a–c], the most convenient laboratory preparation involves a reaction between sulphur dichloride and sodium fluoride in the presence of acetonitrile[82a].

$$3SCl_2 + 4\ NaF \xrightarrow{MeCN} S_2Cl_2 + SF_4 + 4\ NaCl \qquad \text{Eq. 2.2}$$

Since the above reaction is not very suitable for the preparation of [^{35}S]–sulphur labelled sulphur tetrafluoride, the alternative method used in this work for this preparation is based on the fluorination of the elemental sulphur by iodine pentafluoride according to the following equation[82c].

$$5\,S + 4IF_5 \xrightarrow{200\ ^{\circ}C} 5\,SF_4 + 2\,I_2 \qquad \text{Eq. 2.3}$$

The procedure was carried out by loading a stainless steel pressure vessel (60 ml) with a stoichieometric amount of sulphur (0.72 g, 6.6 mmol) according to the equation 2.3. A preweighed quantity (4.0 g, 18.0 mmol) of purified iodine pentafluoride was condensed under vacuum into the vessel. The vessel was then heated for 5 hours at 100 °C followed by 200 °C for 48 hours.

After allowing the vessel to cool to room temperature the volatile material was distilled from -80 °C to -190 °C. The infrared spectrum of the volatile material at this stage showed the presence of sulphur tetrafluoride, thionyl fluoride and silicon tetrafluoride.

The sulphur tetrafluoride was purified by making the adduct $SF_3^+BF_4^-$ from the reaction between sulphur tetrafluoride and boron trifluoride at -80 °C (dichloromethane/solid CO_2)[25]. Unreacted material was pumped away at this temperature. The decomposition of the adduct was carried out by adding the calculated quantity of dry di-ethyl ether. The sulphur tetrafluoride collected from the decompsition of the adduct was stored in a stainless steel pressure vessel and the infrared spectrum of the gas showed no sign of the presence of any impurities, table 2.4.

Table 2.3

Infrared spectrum of BF_3 cm^{-1}

This work	Literature[83]	Assignment
485 m	480	ν_4
693 s	691	ν_2
885 m	888	ν_1
1449 s	1445	ν_3

Table 2.4

Infrared spectum of SF_4 cm^{-1}

This work	Literature[84]	Assignment
891 s	889	ν_1 A_1
869 s	867	ν_6 B_1
730 vs	728	ν_8 B_2
550 w	558	ν_2 A_1
530 w	532	ν_7 B_1

2.2.8 Preparation and Purification of Sulphur Chloride Pentafluoride

The method used in this work for the preparation of sulphur chloride pentafluoride is based on the chlorofluorination of sulphur tetrafluoride by chlorine monofluoride in the presence of caesium fluoride according to the following equation[71].

$$SF_4 + ClF \xrightarrow{CsF} SF_5Cl \qquad \text{Eq 2.4}$$

In the absence of caesium fluoride, a high temperature is required[69] but in the presence of caesium fluoride this reaction occurs at room temperature[71].

Caesium fluoride (2.0g, 13.0 mmol) was ground in the inert atmosphere box and placed in a Monel metal pressure vessel (90 ml) equipped with a valve. The vessel was sealed and transferred to the vaccum glass line where it was pumped out and purified, sulphur tetrafluoride (4.0 mmol) was added by vacuum distillation. Following this an equimolar amount of chlorine monofluoride (4.0 mmol) was condensed into the same vessel after it had been connected to the metal line. The mixture was allowed to warm to room temperature and left for 2 hours.

The sulphur chloride pentafluoride was purified by low trap– to– trap distillation at – 80 C° and identified by its infrared spectrum, table 2.5.

Table 2.5

Infrared spectrum of SF_5Cl cm^{-1}

This work	Literature[86]	Assignment
575 w	578	ν_9 C
600 s	601	ν_3 A_1
710 m	707	ν_2 A_1
854 s	854	ν_1 A_1
909 s	909	ν_8 C

2.3 Preparation of Radiochemically Labelled Species

2.3.1 Preparation of [^{36}Cl]- Chlorine Labelled Dichlorine

[^{36}Cl] chlorine labelled Dichlorine was prepared by the reaction of [^{36}Cl] chlorine labelled hydrochloric acid with potassium permanganate solution according to the following equation(85).

$$4\ HCl + KMnO_4 \longrightarrow KCl + MnO_2 + 2\ H_2O + \frac{3}{2}\ Cl_2 \quad \text{Eq. 2.5}$$

The apparatus used for this preparation is shown in figure 2.5 and was assembled in a fumecupboard, it consisted of a round bottom reaction vessel connected to series of cooled traps. Traps B and C were charged with solid potassium permanganate to remove traces of hydrogen chloride. Both were cooled at − 80 °C (dichloromethane/solid CO_2). Traps D and E were cooled at the same temperature and contained phosphorus pentoxide to remove any trace of moisture The liberated dichlorine was collected in vessel F which was equipped with high vacuum stopcocks (J. Young)to enable the vessel to be isolated from the rest of the apparatus. This vessel was cooled to −130 °C (liquid N_2/isopentane). Trap G to which a vacuum water pump was connected, contained phosphorus pentoxide cooled at −80 °C (dichloromethane/solid CO_2). The system was evacuated before use and the operations were carried out in a dry air at reduced pressure.

An aqueous solution of [^{36}Cl] sodium chloride (3 ml, 75 μCi

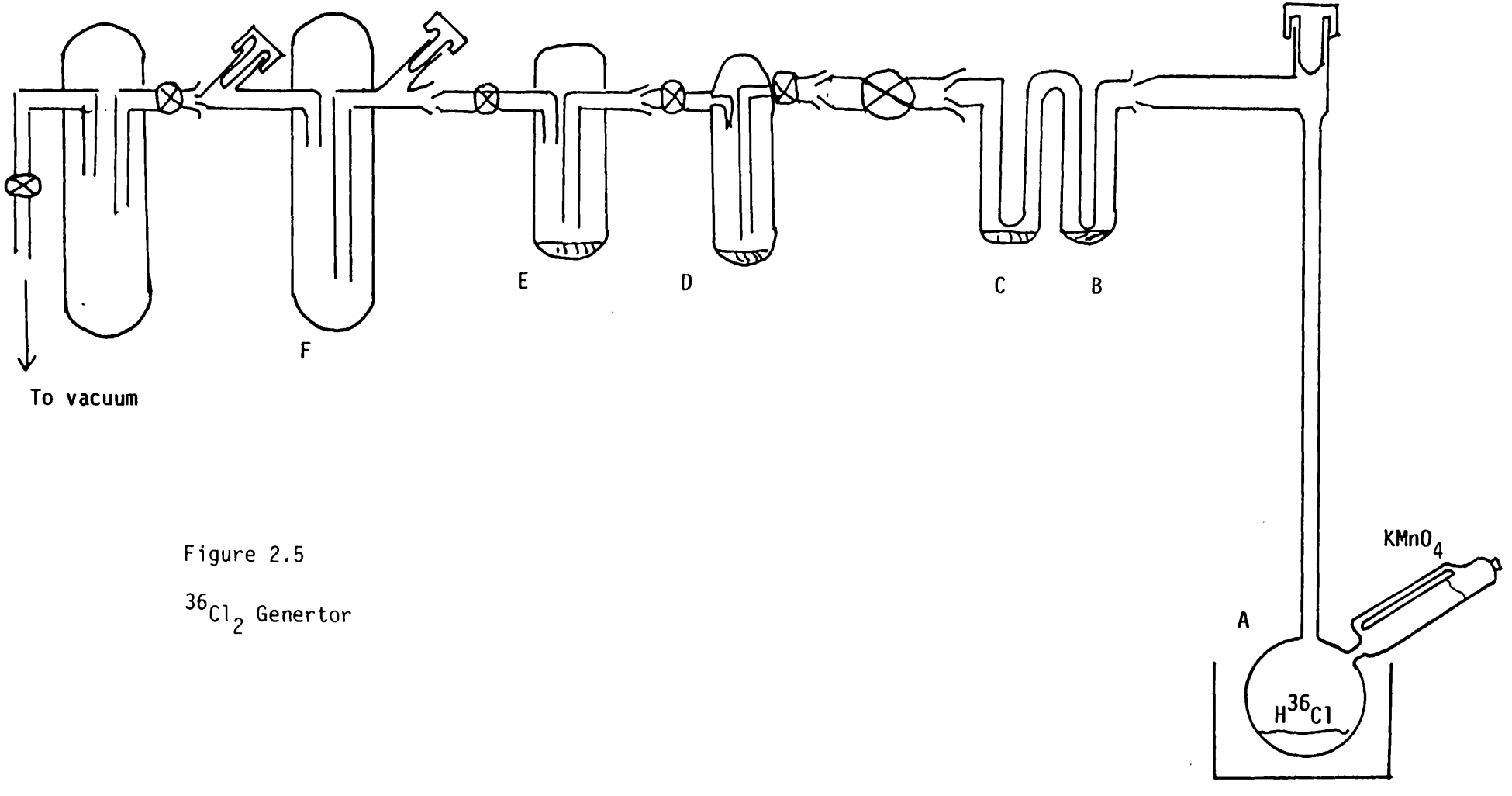


Figure 2.5

$^{36}Cl_2$ Genertor

Amarsham International) was added to concentrated hydrochloric acid (35.4 w/w%, 20 ml) in a beaker. The mixture was then placed in vessel A which was kept at 60 C° by means of a water bath. A solution of potassium permanganate (16g/300ml of water) which had been previously stirred overnight was added to the mixture dropwise with constant stirring. The dichlorine liberated was distilled through traps 1 to 4 and collected in vessel 5 which was then isolated and transferred to the vacuum line where it was degassed at −196 C°, the dichlorine was stored in a Monel metal pressure vessel over phosphorus pentoxide until required.

2.3.2 Preparation of [^{36}Cl]– Chlorine Labelled Chlorine Monofluoride

Labelled chlorine monofluoride was prepared by the same method as that used for the preparation of non labelled chlorine monoflorine. The Monel metal pressure vessel containing [^{36}Cl] di– chlorine was connected to the metal line previously described. Equimolar (8.0 mmol) of [^{36}Cl] di– chlorine and chlorine trifluoride were loaded into the reaction vessel and heated to 155 C°. The process of purification of [^{36}Cl] labelled chlorine monofluoride was identical of that prescribed previously.

2.3.3 Preparation and Purification of [^{36}Cl] Chlorine Labelled Hydrogen Chloride[87]

Gaseous [^{36}Cl] chlorine labelled hydrogen chloride was prepared by the reaction of concentrated hydrochloric acid (35.4 w/w%) with sulphuric acid according to the following equation.

$$H^{36}Cl\ (aq) + H_2SO_4\ (aq) \longrightarrow H^{36}Cl\ (g) + H_2SO_4\ (aq) \quad \text{Eq. 2.6}$$

The apparatus used for this preparation is shown in figure 2.6. A mixture of [^{36}Cl] chlorine labelled sodium chloride (2.5 ml, 62.5 μCi Amarsham International) and concentrated hydrochloric acid (35.4 w/w%, 10 ml) was added dropwise to concentrated sulphuric acid. An iron bar sealed in glass was used to stir the reactants in the reaction vessel. The [^{36}Cl]- chlorine labelled hydrogen chloride generated was passed through a series of cooled traps containing phosphorus pentoxide and connected to the reaction vessel via a pressure equilibrating arm. Traps 1 and 2 were cooled to $-80\ ^{\circ}C$. Gaseous [^{36}Cl] chlorine labelled hydrogen chloride was collected in a vessel 3 cooled to $-130\ ^{\circ}C$ (liquid N_2/isopentane). The vessel was equipped with high vacuum stopcocks (J. Young) so that it can be isolated from the rest of the apparatus.

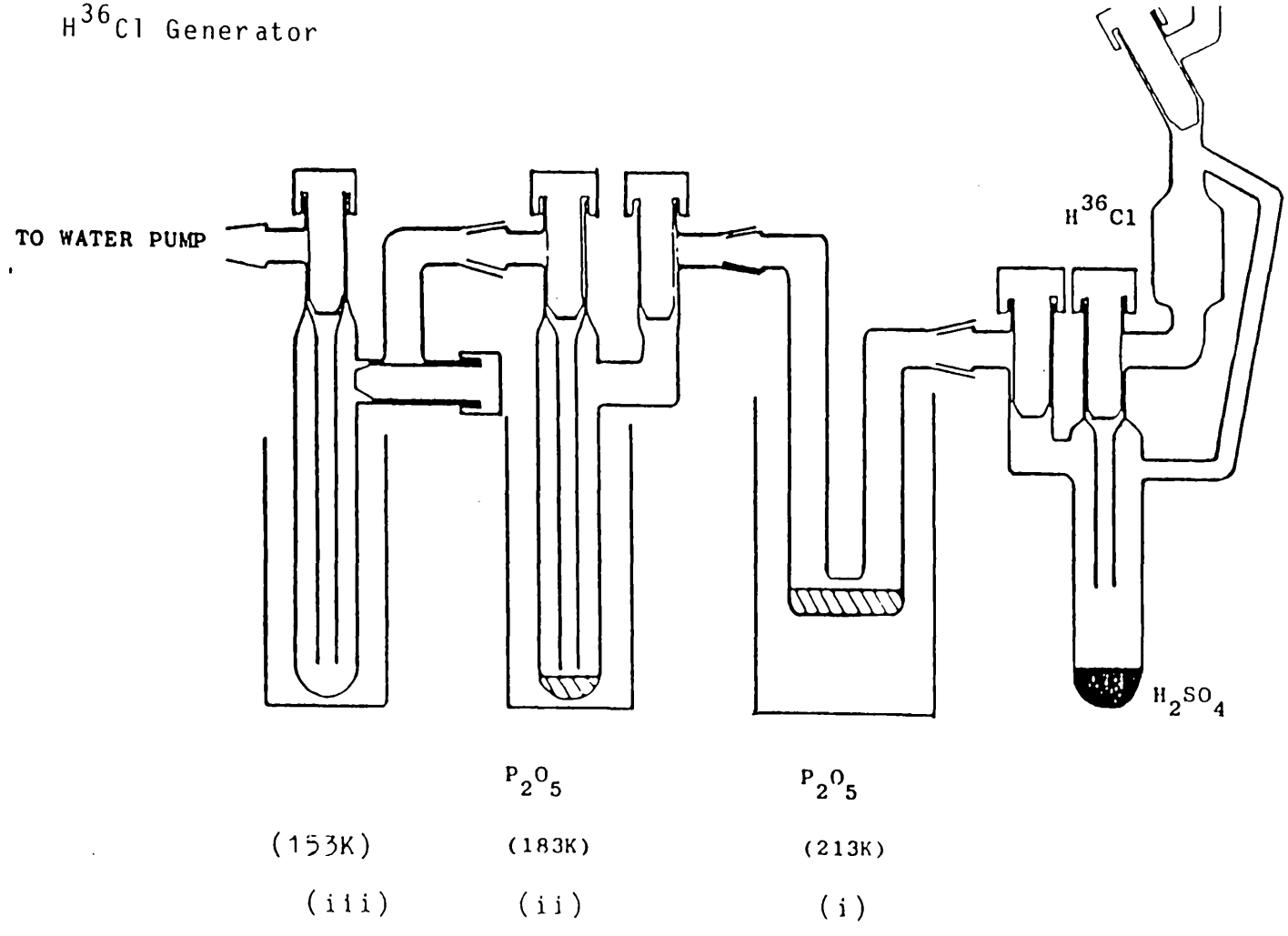
Once the reaction was finished, the collection vessel was isolated from the rest of the apparatus and transferred to the glass vacuum line where it was degassed at $-196\ ^{\circ}C$. The [^{36}Cl] chlorine labelled hydrogen cloride was stored over phosphorus pentoxide in a stainless steel pressure vessel.

2.3.4 Preparation and Purification of [^{35}S] Labelled Sulphur Tetrafluoride[82c]

The method described before for the preparation of non labelled sulphur tetrafluoride was used as a basis for the radio-chemical preparation. The dilution of rhombic [^{35}S] sulphur was carried out by

Figure 2.6

$H^{36}Cl$ Generator



mixing it with a solution of S_8 according to the following procedure. Dry carbon disulphide, CS_2, was added to a Monel metal pressure vessel containing inactive rhombic sulphur. The carbon disulphide was also added to the ^{35}S container using a long needle. Subsequently, this solution was transferred to the Monel metal pressure vessel using the same needle. The container was washed several times with carbon disulphide and the washing was also transferred to the same vessel. The carbon disulphide was removed under vacuum and the preweighed quantity of purified iodine pentafluoride was added by vacuum distillation. The reaction time and the purification procedure were identical to those described above.

2.4 Radiochemical Techniques

Radiotracer techniques are widely used in heterogeneous catalysis. Their main advantage is the high sensitivity for the detection of even a small quantity of species present on the surface of the solid. Both strongly and weakly adsorbed species can be detected and differentiated quantitatively.

2.4.1 Choice of Isotope

The choice of the isotope is generally based on the following factors

— The availability of the isotope.

— The length of its half life.

— The ease of detection and the ease of handling.

The radio isotopes used in this work were ^{36}Cl and ^{35}S. The radio

isotope ^{36}Cl decays by β^- emission with a maximum energy equal to 0.714 MeV and half life equal to 3×10^5 years(88).

$$^{36}_{17}Cl \longrightarrow {}^{36}_{18}Ar + {}^{0}_{-1}\beta \qquad \text{Eq. 2.7}$$

The radio isotope ^{35}S decays by β^- emission with a maximum energy equal to 0.167 MeV and half life equal to 87.2 days(89).

$$^{35}_{16}S \longrightarrow {}^{35}_{17}Cl + {}^{0}_{-1}\beta \qquad \text{Eq. 2.8}$$

The β^- particles are electrons ejected from the nuclei of the isotope according to the equation 2.9.

$$^{1}_{0}n \longrightarrow {}^{1}_{1}P^{+} + {}^{0}_{-1}e^{-} \qquad \text{Eq. 2.9}$$

In this process, the mass number remains unchanged while the atomic number increases by one unit. Both isotopes were counted using a Geiger Müller counter.

2.4.2 Geiger Müller Counter

The Geiger Müller counter used for counting ^{36}Cl and ^{35}S labelled compounds consists of an earthed cylindrical metal tube, filled with a mixture of argon and an organic substance, such as methane which is used as a quench gas. The inside wall of the cylinder acts as the cathode and the anode is a coaxial wire suspended along the tube. The tube is fitted at

one end with a thin mica window and connected to a scaler.

When particles such as alpha or beta pass through the mica window, the gas inside the tube interacts with these particles leading to a partial ionisation of the gas which produces a large number of ion pairs. The electrons formed move rapidly towards the wire and the positive ions formed drift relatively slowly towards the wall. The pulse resulting from the ionisation event is recorded by the electronic scaler as an output, proportional to the strength of the initial ionising radiation.

2.4.3 Plateau Curve

In a Geiger Müller counter, the free electrons formed move towards the anode with a velocity depending on the voltage applied. However, counts are not recorded until the applied voltage reaches a threshold point at which the voltage is sufficient to attract the free electrons to the anode. Once this point is reached, the count rate rises rapidly as the voltage increases until the plateau curve is reached where the count rate arising from a given radiation source is independent of the applied voltage.

The first positive ions reaching the cathode cause secondary electron emission from the surface which is then led to the generation of spurious discharge inside the counter. For this reason, the plateau region is never completely flat. This secondary emission is supressed by a quench gas.

As the potential increases, a break down of the self quenching mechanism occurs since the quench gas cannot cope with the large number

of spurious discharges. Thus self discharge of the counter occurs and the count rate begins to rise at the end of the plateau region.

The plateau curves of all Geiger Müller counters used in this work were determined using ^{137}Cs as a source of radiation. A plot of count rate versus voltage was obtained and a typical curve is shown in figure 2.7. The working voltage was set in the middle of the plateau region. A plateau curve was determined for every Geiger Müller counter used throughout this work.

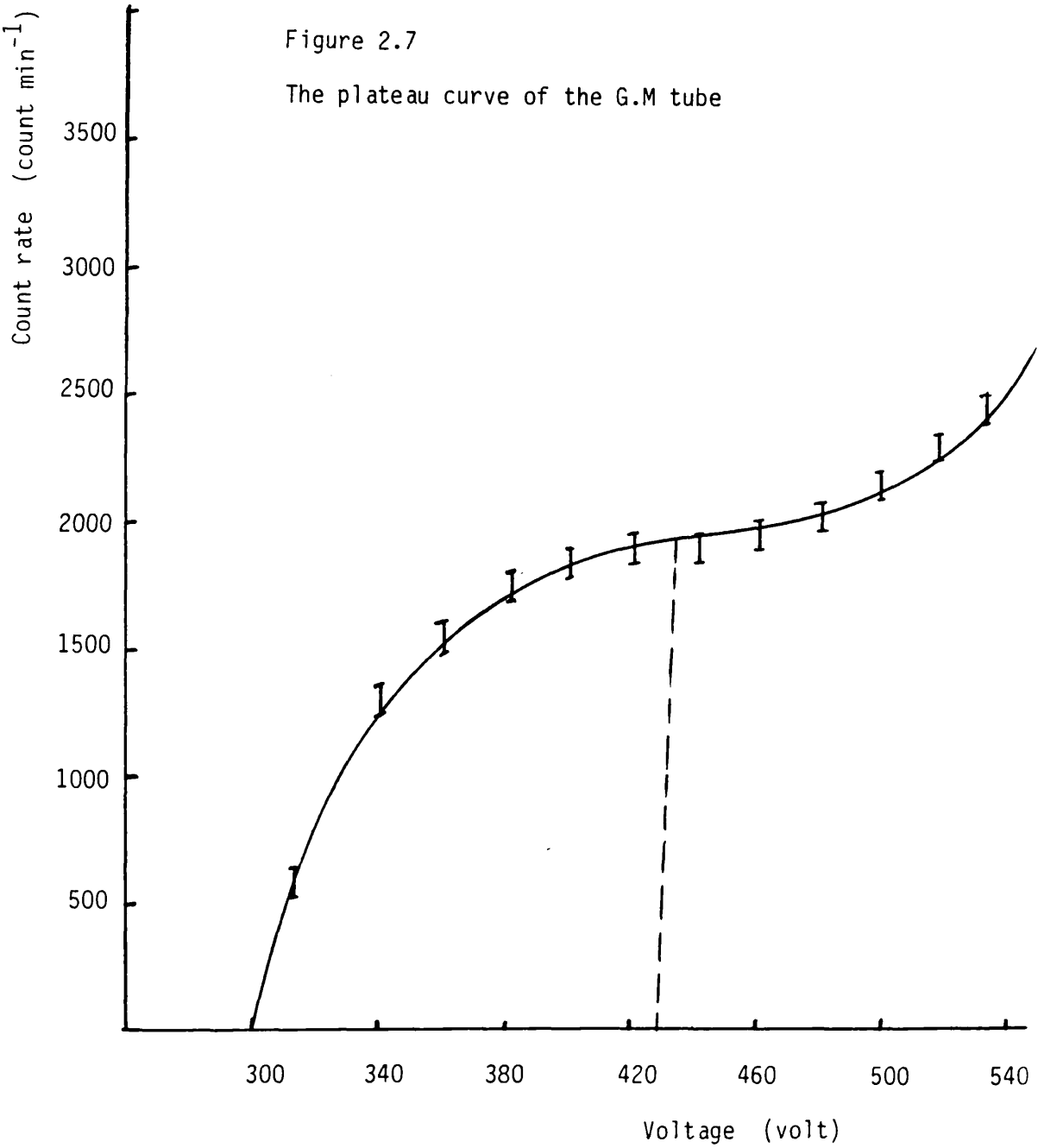
2.4.4 Dead Time

In a Geiger Müller counter, the motion of the positive charges is very slow compared with the negative charges (free electrons). Immediately after a collection of electrons, the central wire is surrounded by sheath of positive ions which has the effect of reducing the electrical field near the anode. Whilst the anode is surrounded by the positive ions, the counter can not record another pulse. During the period in which the positive ions migrate to the cathode, the counter can not detect any particles passing through it.

This insensitive period is known as the dead time of the Geiger Müller counter. In accurate counting experiments, a correction is necessary for counts lost in such periods especially when the count rate is high. The true count rate N(t) is related to the observed count rate N(0) by the following relation.

Figure 2.7

The plateau curve of the G.M tube



$$N(t) = \frac{N(0)}{(1 - N)\ \tau} \qquad \text{Eq. 2.10}$$

Where τ is the dead time

A sample of [^{18}F] fluorine labelled caesium fluoride was used for the determination of the dead time for the Geiger Müller tubes used in this work. The process was carried out by counting the sample over three half lives.

The decay of a radioisotope follows equation 2.11

$$A(t) = A_0\ e^{-\lambda t} \qquad \text{Eq. 2.11}$$

where λ = decay constant

$A(t)$ = activity of sample at time t

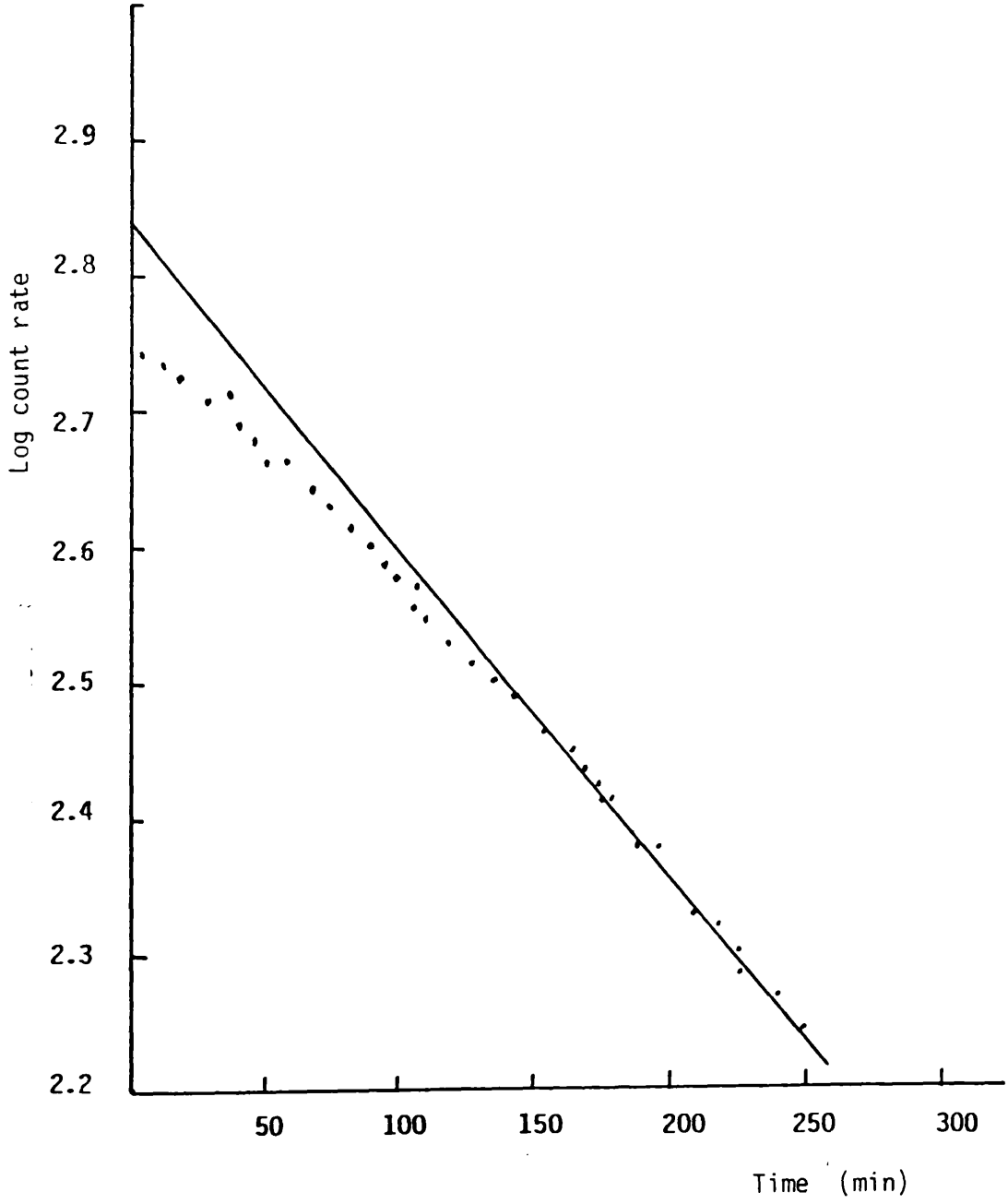
A_0 = activity of sample at time t = 0

Consequently, the plot of ln A(t) versus time should be a straight line with a gradient $-\lambda$ and intercept ln A_0. The plot of ln A(t) versus time obtained, figure 2.8, showed a linear relationship at $t > 250$ minutes, that is at low activity and was nonlinear at $t < 250$ minutes, that is at high activity where the effect of the dead time is significant.

The extrapolation of the linear portion to time $t = 0$, using the half life of ^{18}F (109.72 ± 0.06 minutes) gave the true cont rate N(t), which is related to the observed count rate N(0) by the equation 2.10. The dead time was calculated for the first twenty points on the graph, and the mean

Figure 2.8

The dead time of the G.M tube; decay of fluorine-18



value was taken to be the dead time of the system.

2.4.5 Background Correction

In the absenee of any radioactive source a Geiger Müller counter will register some counts. These are due to, the existance of random radiation in the atmosphere, cosmic radiation emitted to the earth atmosphere and material used in the construction of laboratory. These undesirable radiations affect the radio–chemical analysis particularly at low activity of a radioactive source where the background count rate is appreciable. This effect can be reduced by counting the sample in a shielded container.

The experiments which involved counting of ^{36}Cl and ^{35}S were performed in a reaction glass vessel, which could not be shielded. Therefore, it was necessary to correct any reading given by the counter for the background according to the relation,

$$C_t = C_o - C_b \qquad \text{Eq. 2.12}$$

where C_t = true count

C_o = observed count

C_b = back ground count

2.4.6 Statistical Errors

The number of disintegrations observed from a constant radioactive source in a given period of time is not constant, due to the random nature of the decay process. The probability W(m) of obtaining m disintegrations

in time t from N_0 atoms is given by the expression[90].

$$W(m) = \frac{N_0!}{(N_0 - m)!\ m!} P^m(1-p)^{N_0-m} \qquad \text{Eq. 2.13}$$

where P is the probability of a disintegration occuring within the time of observation.

The expected standard deviation σ for the number of radioactive disintegration is given by the expression

$$\sigma = \sqrt{me^{-\lambda t}}$$

In normal counting practice, the observation time t is small in comparison with the half life. Thus the standard deviation σ can be given by

$$\sigma = \sqrt{m} \qquad \text{Eq. 2.14}$$

where m is the number of counts obtained.

2.4.7 ^{36}Cl and ^{35}S Counting Apparatus

Radiochemical measurement techniques used in this work were monitored using the apparatus shown in figure 2.9. This apparatus consisted of a reaction vessel constructed from Pyrex glass and designed to facilitate the access of radiochemical gases and the handling of solids sensitive to

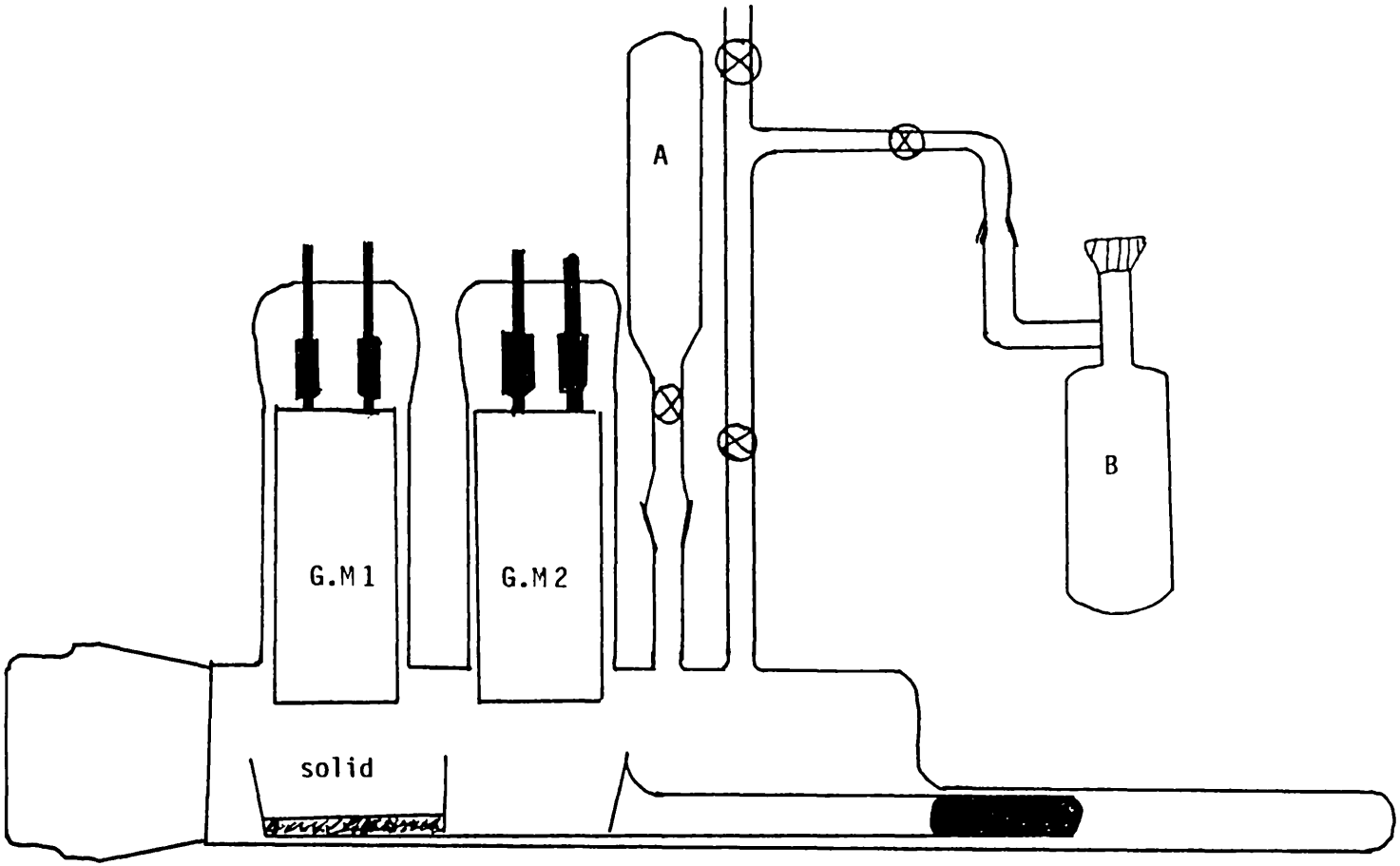


Figure 2.9 Counting cell

moisture.

The reaction vessel was attached to the vacuum line system and can be isolated from the rest of the apparatus by using a high vacuum stopcock (Rotaflo). The main components of this apparatus are the two Geiger Müller tubes. These were mounted on the reaction vessel to enable the surface radioactivity to be determined directly. These tubes were kept at the same height to ensure an identical counting geometry for each of the Geiger Müller tubes. Inside the reaction vessel was a Pyrex glass boat, in which the solid sample was loaded through a B14 socket to which an ampoule containing the solid sample was connected. The boat ended with a magnet bar sealed in glass. The boat can be moved along the length of the reaction vessel by using a magnet.

The characteristics of the Geiger Müller tubes counting vary slightly from a tube to another. Therefore, count rate given by two Geiger Müller tubes held in the same conditions are slightly different. However, any set of Geiger Müller tubes used in this work was intercalibrated regularly. These were performed by admitting different pressures of a radioactive gas and recording the count for each of the Geiger Müller tubes at every pressure.

The intercalibration factor was obtained by constructing a plot of Geiger Müller tube 1 count rate versus Geiger Müller 2 count rate. A typical example obtained with $[^{36}Cl]$–HCl, as a radioactive source, is shown in figure 2.10 and tabulated in table 2.6. The gradient of the straight line is equal to the intercalibration factor typically 1.16.

Figure 2.10

Geiger Müller 1 count rate Vs Geiger Müller 2 count rate

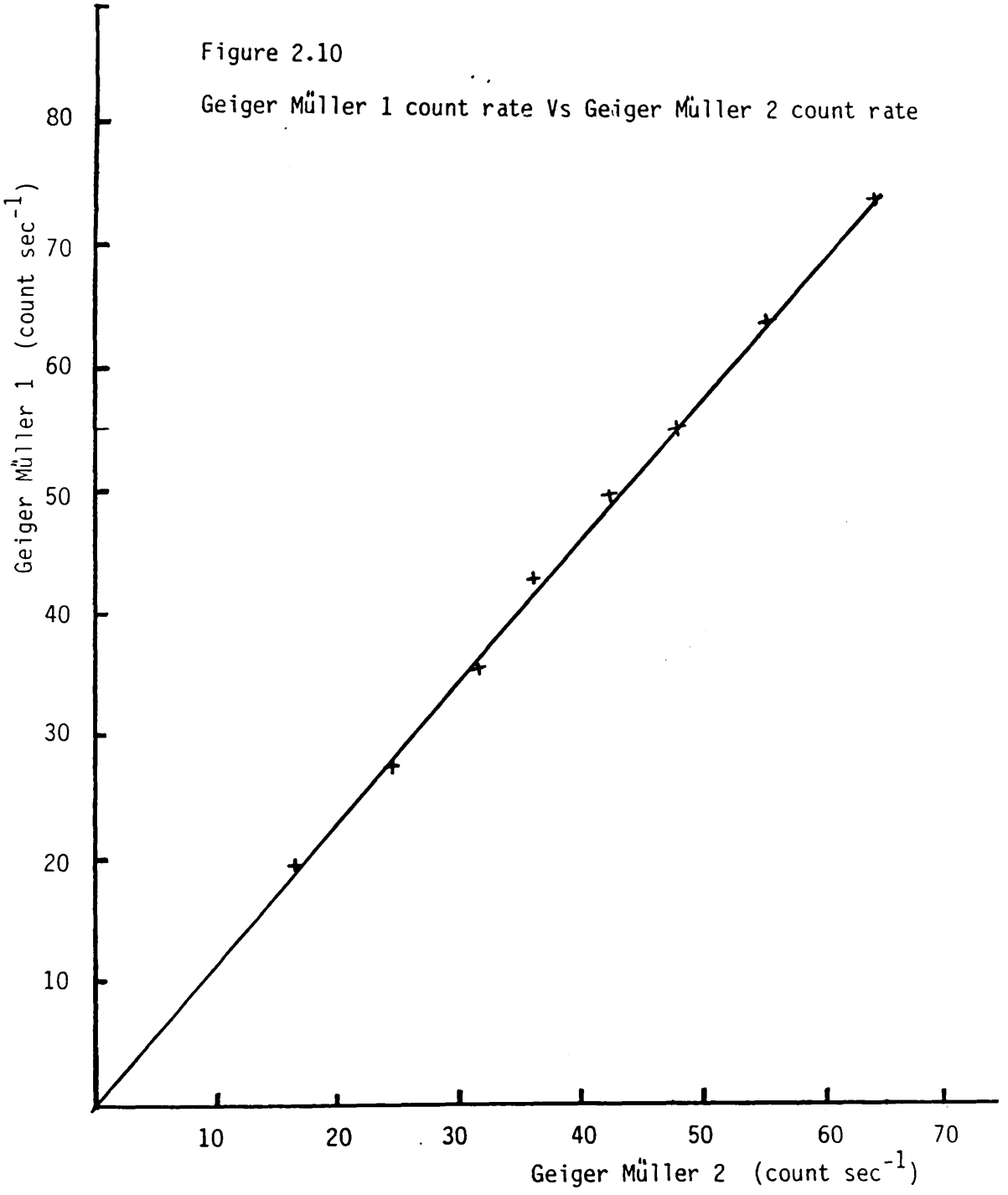


Table 2.6

[^{36}Cl]-HCl pressure versus counte rate

Pressure	Geiger Müller Tube 1 Count rate	Geiger Müller Tube 2 Count rate
Torr	count sec^{-1}	count sec^{-1}
21.02	20.06 ± 0.18	17.24 ± 0.16
29.73	28.11 ± 0.21	24.13 ± 0.20
42.61	35.75 ± 0.26	31.03 ± 0.22
65.41	43.05 ± 0.26	37.06 ± 0.24
81.24	49.79 ± 0.28	43.10 ± 0.26
96.51	55.20 ± 0.30	47.41 ± 0.28
117.58	64.04 ± 0.32	55.17 ± 0.30
144.88	73.69 ± 0.35	63.79 ± 0.32

More details of the manipulation procedure for the gas solid system will be described in a next chapter.

CHAPTER THREE

CHAPTER THREE

Activation of Metal Fluorides and B.E.T area Determinations

Introduction

The specific surface area of a solid is one of the parameters that must be determined if any detailed understanding of its behaviour as catalyst is required. In this work, surface areas were determined using the B.E.T method. In this method, surface areas are normally measured by determining the amount of gas adsorbed on the solid, at a given temperature as a function of pressure[91].

For solids having large surface areas, nitrogen was used as adsorbate. For solids of small surface areas, that is less than 5 m^2g^{-1}, the radioisotrope [^{85}Kr] krypton was used as adsorbate, the advantage being that a small change in the pressure can be detected relatively precisely[92].

The pretreatment given to a sample was found to have a great effect in determing its B.E.T area. pretreatment generally increases the B.E.T area and enhances catalytic activity[71,92].

Caesium fluoride has been treated in different ways. Pretreatment with hexafluoroacetone in the presence of acetonitrile was found to be the best way of increasing its surface area[92]. In the present work this

method was also applied to mercury(II) fluoride and B.E.T areas of solids after various treatments were determined.

3.1 Activation of Metal Fluorides

3.1.1 Activation of Caesium Fluoride by Treatment with Hexafluoroacetone in the Presence of Acetonitrile

Caesium fluoride was activated by treatment with hexafluoroacetone in the presence of acetonitrile according to the following reaction scheme[93].

$$CsF_{(s)} + (CF_3)_2CO(g) \underset{\longleftarrow}{\xrightarrow{MeCN}} Cs^+(solv) + (CF_3)_2FCO^-(solv) \quad \text{Eq. 3.1}$$

$$Cs^+(CF_3)_2FCO^-(s) \xrightarrow[48\ h]{125\ ^oC} CsF_{(s)} + (CF_3)_2CO_{(g)} \quad \text{Eq. 3.2}$$

The experimental procedure was carried out as described in the literature[92].

Caesium fluoride (4.0 g, 26.0 mmol B.D.H. Optran grade) was ground in an agate pestle and mortar in an inert atmosphere box. The sample was placed in a stainless steel pressure vessel containing four stainless steel ball bearings. After sealing the vessel, it was transferred to the vacuum line. The sample was evacuated and, subsequently, dried acetonitrile (5 cm^3) and hexafluoroacetone (30.0 mmol) were added. The mixture was allowed to warm to room temperature and shaken for 12 hours. Unreacted hexafluoroacetone and acetonitrile were removed by

vacuum distillation. The infrared spectrum of the solid at this stage is shown in table 3.1. The infrared spectrum of hexafluoroacetone is presented in table 3.2. The adduct formed was then thermally decomposed at 120 °C for 48 hours.

3.1.2 Activation of Mercury(II) Fluoride by Treatment with Hexafluoroacetone in the Presence of Acetonitrile

Mercury(II) fluoride, a commercial product, used in this work was yellow. The activation process involved treatment with hexafluoroacetone in the presence of acetonitrile and was the same as that used for caesium fluoride.

Mercury(II) fluoride (4.0 g, 16.8 mmol) was well ground in an inert atmosphere box, and placed in a stainless steel pressure vessel containing four ball bearings. The vessel was evacuated and acetonitrile (7 cm^3) and hexafluoroacetone (34.0 mmol) were added successively by vacuum distillation. The mixture was allowed to warm to room temperature and was left shaking overnight. Unreacted hexafluoroacetone and acetonitrile were then removed. The infrared spectrum of the solid at this stage is summarized in table 3.3.

The vessel containing the sample was connected to the vacuum line via a U− shaped glass vessel equipped with two Young's high vacuum stop cocks, figure 3.1. The thermal decomposition of the adduct formed was carried out at 80 °C for 12 hours, and the volatile material liberated from the decomposition was collected in the U− tube, which was cooled to

Table 3.1

Infrared spectrum of $Cs^+(CF_3)FCO^-$ (cm^{-1})

This work	Literature[94]	Assignment
1455 m	1450	ν CO
1345 w	1350	ν CF
1250 s	1250	ν CF
1215 s	1210	ν CF
1155 s	1150	ν CF
1100 s	1100	ν CF
960 s	960	ν CC
785 w	780	ν CC
735 w	730	δ CF
635 w	630	δ CF

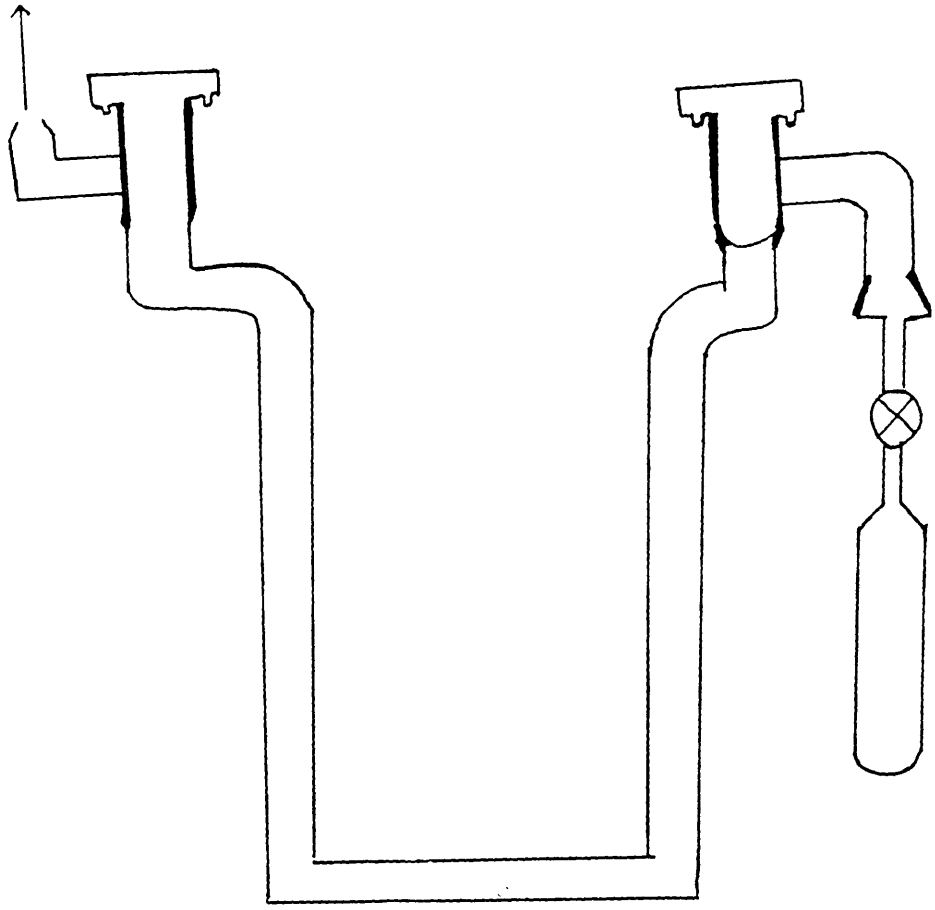
Table 3.2

Infrared spectrum of $(CF_3)_2CO$ cm^{-1}

This work	Literature[95]	Assignment
1805 m	1805	ν CO
1340 s	1340	ν CF
1270 w	1265	ν CF
1220 s	1250	ν CF
970 s	970	ν CC
780 w	780	ν CC
720 s	720	δ CF
	640	δ CF

Figure 3.1

A ⌐¬ vessel



$-196\ ^{\circ}C$ (liquid N_2). The infrared spectrum of the volatile material is shown in table 3.4. The bands obtained were the same as the hexafluoroacetone before reaction. The infrared spectrum of the solid remaining after decomposition showed no evidence for the presence of any band attributable to the adduct, therefore the adduct appeared to be completely decomposed. Mercury(II) fluoride remaining after decomposition was bright yellow.

In order to verify the mass balance, a known quantity of the adduct formed was placed in a Monel metal pressure vessel and thermally decomposed as described above. This procedure was repeated three times on different fresh activated sample. Data for mass balance of the thermodecomposition were obtained; the results are summarized in table 3.5.

3.1.3 Pretreatment of Mercury(II) Fluoride with Sulphur Tetrafluoride

Mercury(II) fluoride (3.0 g, 12.0 mmol) was ground and placed in a stainless steel pressure vessel in an inert atmosphere box. The vessel was evacuated and SF_4 (6.0 mmol) was added by vacuum distillation. The material was allowed to react at room temperature for 16 h. After removing the volatile material at room temperature, the solid remaining was colourless. The infrared spectrum of the volatile material showed the presence of thionyl fluoride, silicon tetrafluoride and sulphur tetrafluoride, table 3.6.

Table 3.3

Infrared spectrum of the solid formed by reaction of HgF_2 with $(CF_3)_2CO$ (cm^{-1})

1700	m	ν CO
1330	W	ν CF
1225	S	ν CF
1100	S	ν CF
1050	W	ν CF
980	S	ν CC
780	W	ν CC
730	W	δ CF

Assignments were obtained by analogy with $Cs^+(CF_3)_2FCO^-$

Table 3.4

Infrared spectrum of the volatile material collected from the decomposition of the solid formed by reaction of HgF_2 with $(CF_3)_2CO$

1805	m	ν CO
1340	S	ν CF
1270	W	ν CF
1220	S	ν CF
970	S	ν CC
780	W	ν CC
720	S	δ CF

Table 3.5

Mass balance, assuming the adduct stocheiometry is $HgF_2.2(CF_3)_2CO$ and the solid is HgF_2.

Solid prior to thermal decomposition	Solid after thermal decomposition		Decrease in mass		$(CF_3)_2CO$ collected		Mole ratio HgF_2 : $(CF_3)_2CO$
g	g	mmol	g	mmol	g	mmol	
1.00	0.41	1.72	0.59	3.55	0.59	3.55	2.06
1.56	0.67	2.81	0.89	5.36	0.88	5.30	1.88
2.00	0.84	3.52	1.16	6.98	1.17	7.04	2.00

Table 3.6

Infrared spectrum of the volatile material after treatment of HgF_2 with SF_4

This work

SF_4	SOF_2	SiF_4
	1335 s	
		1020 s
890 s		
870 s		
	808 s	
	748 vs	
730 vs		
550 w		
	530 s	

Literature

SF_4[96,97]	SOF_2[97]	SiF_4[97]
	1333 ν_1	
		1010 ν_3
889 $\nu_1 A_1$		
867 ν_6		
	808 ν_2	
	748 ν_5	
728 ν_8		
	530 ν_3	
523 ν_7		
463 ν_3		
	390 ν_6	

3.2 B.E.T Area Determination

3.2.1 Introduction

When a solid is exposed in a closed space to a gas or vapour, the solid may adsorb the gas. This adsorption is a consequence of the field force at the surface of the solid, which attracts the molecules of the gas. The forces of attraction, emanating from the solid are two main kinds, physical and chemical, and they give rise respectively to physical adsorption and chemisorption. Chemisorption involves the formation of chemical bonds between the adsorbent and the adsorbate. In consequence, chemisorption is limited to the formation of a monomolecular layer at the surface of the solid. Unlike chemisorption, no chemical bonds are formed in physical adsorption, and forces of the Van der Waals type are involved. Therefore, this type of adsorption would be occurring between all gases and solids provided the temperature is not considerably in excess of the boiling point of the adsorbate. Multilayers may be built up on the surface.

The extent of coverage of the surface by the adsorbate will be related to the pressure of the adsorbate gas. Thus if a method of determining when the adsorbed monolayer is complete can be found, and the cross–sectional area of the gas molecule in the adsorbed state is known, the total surface area of the adsorbent presented to the gas phase can be calculated.

The adsorption isotherm is the function which relates, at constant

temperature, the amount of substance adsorbed to an adsorbate pressure in the gas phase. This adsorbed amount can be expressed as a number of moles or as the corresponding volume. If the gas is below its critical point, the adsorbed amount is given by the equation.

$$x = f\left(\frac{p}{p_0}\right) \qquad \text{Eq. 3.3}$$

where x = the amount adsorbed.

$\frac{p}{p_0}$ = the relative pressure.

The adsorbed amount corresponding to a monolayer of gas on the surface can be determined using the B.E.T equation, shown below.

Brunauer, Emmett and Teller focussed attention on the process of interchange of molecules between the gas phase and the adsorbed film, thereby following the path laid down by Langmuir[98], who regarded the surface of the solid as an array of adsorption sites, each site being capable of adsorbing one molecule. A state of dynamic equilibrium was postulated, in which the rate at which molecules arriving from the gas phase and condensing on to bare sites is equal to the rate at which molecules evaporate from occupied sites.

Brunauer, Emmett and Teller explicitly extended Langmuir's treatment to second and higher molecular layers[91] on the basis of many assumptions. This led to the following simple equation called the B.E.T equation.

$$V = \frac{V_m C P}{(p_0 - p)\left\{ 1 + (C-1)\frac{p}{p_0} \right\}} \qquad \text{Eq. 3.4}$$

where

V: The total volume adsorbed

V_m: The volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer.

$$C = e^{(E_1 - E_L)RT}$$

E_1: is the heat of adsorption in the first layer.

E_L: is the heat of liquefaction of the adsorbate.

3.2.2 B.E.T Area Determination of Caesium Fluoride Activated by Hexafluoroacetone in the Presence of Acetonitrile

Surface areas were determined by the B.E.T method using the radioisotope ^{85}Kr as adsorbate. The number of Kr molecules adsorbed x was calculated from the equation.

$$x = \frac{P}{T} \frac{\Delta V}{R} \frac{N}{760 \times 10^3} \frac{1}{} \qquad \text{Eq. 3.5}$$

where P = pressure (Torr)

ΔV = change in volume (cm^3)

N = Avogadro number (6.022×10^{23})

T = temperature at which adsorption isotherm is determined (K)

R = gas constant (cm^3 Torr K^{-1} mol^{-1})

The surface area was determined by making use of the B.E.T equation in the form.

$$\frac{P}{x(P_0-P)} = \frac{1}{X_m C} + \frac{C-1}{X_m C}\frac{P}{P_0} \qquad \text{Eq. 3.6}$$

where x = amount adsorbed at pressure P

P_0 = saturated vapour pressure of the gas at the adsorption temperature

C = constant for any particular gas/solid system

X_m = quantity of gas required to form a monolayer

from this equation the plot of $\frac{P}{x(P_0-P)}$ versus $\frac{P}{P_0}$ should give

a straight line with slope equal to $\frac{C-1}{X_m C}$ and intercept of $\frac{1}{X_m C}$

The surface area was then calculated from the following expression

$$\text{Surface Area} = \frac{X_m A}{W} \; m^2.g^{-1} \qquad \text{Eq. 3.7}$$

where A = the molecular area of the gas adsorbed, that is Kr

W = weight of sample

The quantity X_m was determined using equation 3.8

$$X_m = \frac{1}{S + i} \qquad \text{Eq. 3.8}$$

where S = slope

i = intercept

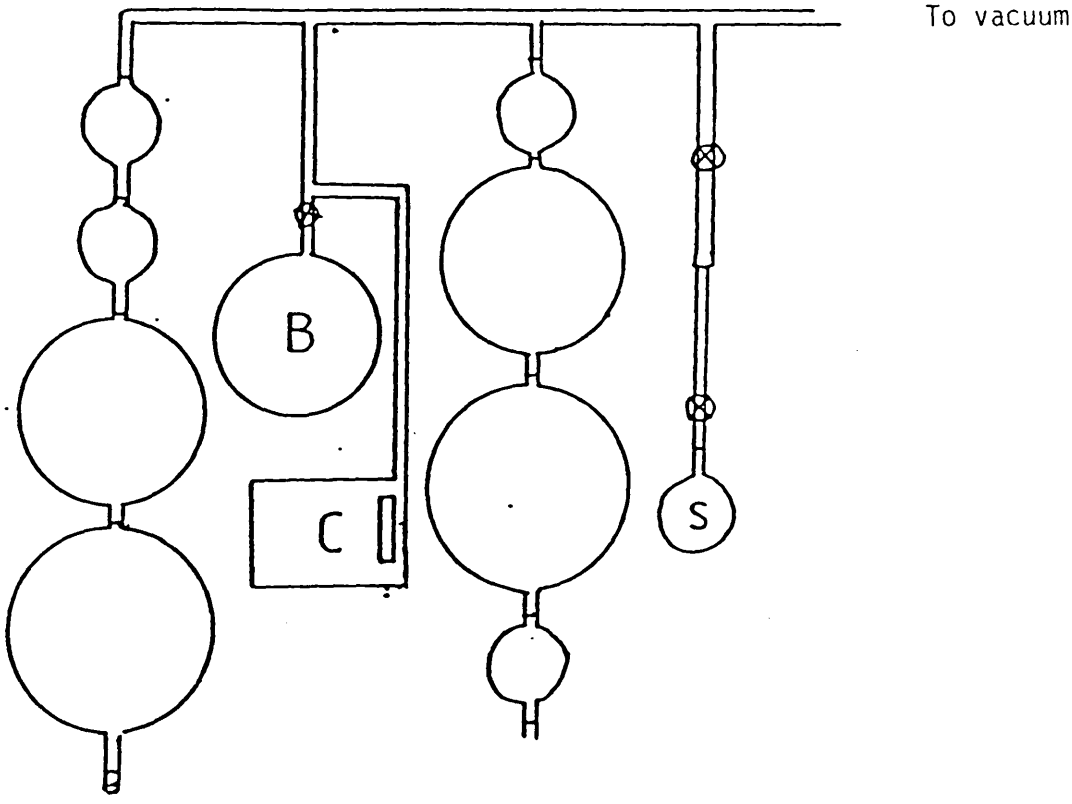
Both S and i can be deduced from the experimental data.

The apparatus used for this B.E.T area determination was similar to that described by Aylmore and Jepson[99] modified to facilitate the handling of the hygroscopic material. The apparatus consisted of a calibrated Pyrex glass section comprising two sets of bulbs, each attached to a mercury reservoir, a ^{85}Kr storage bulb (B), a thin-walled counting vessel (C) and the adsorbent sample bulb (S), figure 3.2. The system was also equipped with reservoirs containing the radioisotope ^{85}Kr and inactive Kr.

A desirable working activity was achieved by diluting the radioisotope ^{85}Kr with inactive Kr. This dilution was carried out by condensing an appropriate amount of ^{85}Kr and inactive Kr into a trap containing charcoal activated at 300 °C under vacuum. The diluted sample was left for 12 hours at 196 °C to equilibrate.

Figure 3.2

B.E.T apparatus



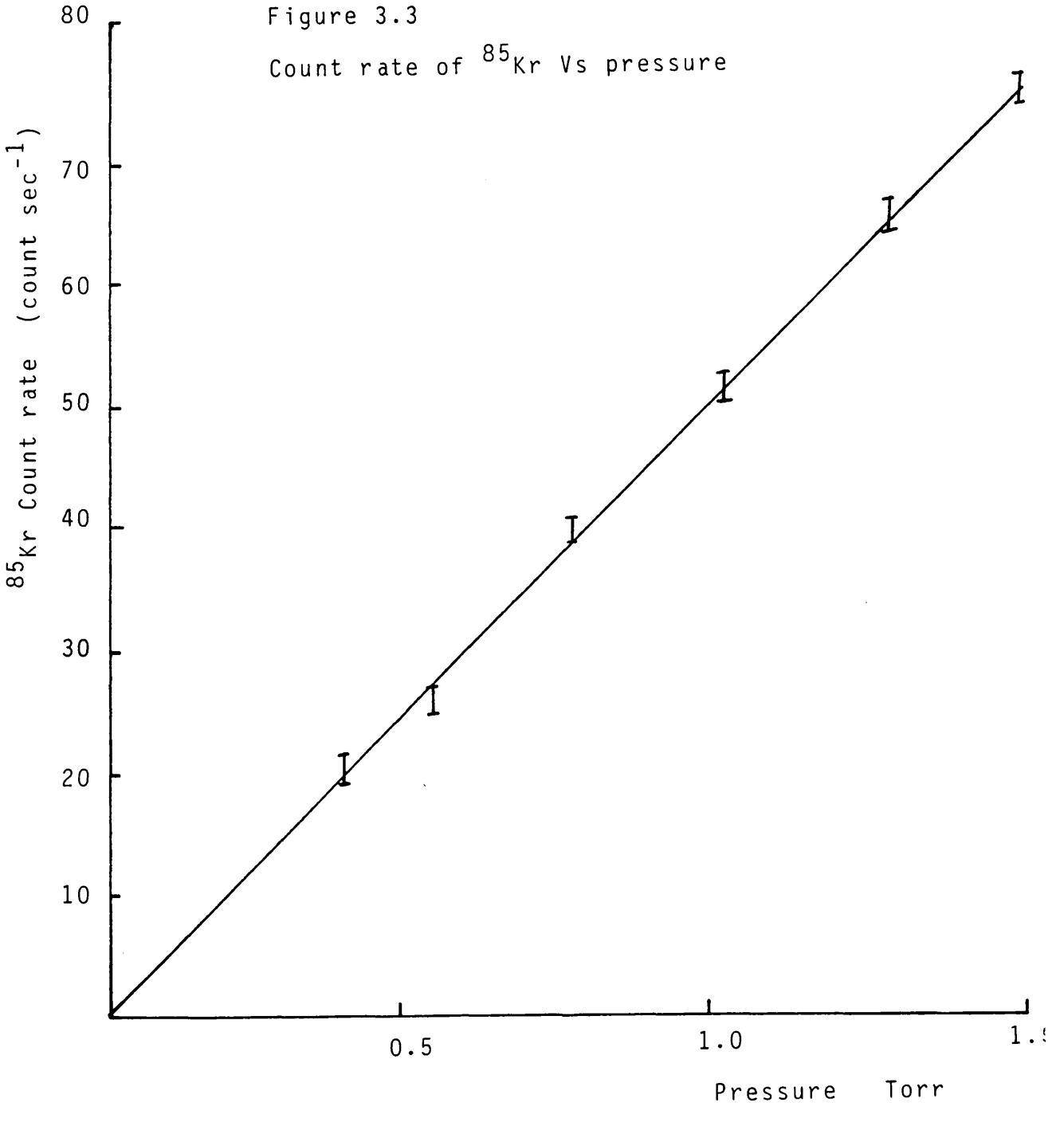
A calibration curve of ^{85}Kr count rate versus pressure was determined, figure 3.3. Pressures were measured using a Pirani gauge and ^{85}Kr activities were determined using a Geiger Müller counter, mounted externally immediately below the counting vessel (C). The time of counting was adjusted to give a total count of $> 10^4$ to minimise counting errors. After each pressure change, twenty minutes were required for equilibrium to be attained.

The sample bulb (S) was loaded with an accurately weighed sample (0.2−0.3 g, 1.3−1.9 mmol) of caesium fluoride in an inert atmosphere box. The sample was sealed and transferred to the vacuum line where it was evacuated overnight.

The bulbs were filled with mercury and ^{85}Kr was admitted to the manifold from the storage bulb (B). Changes in pressure were obtained by varying the mercury volume in the bulbs. The relation between ^{85}Kr count rate and volume, and hence between pressure and volume at room temperature was determined. For each surface area determination, a plot of volume versus (temperature/pressure) was constructed and gave a straight line with an intercept on the Y axis corresponding to the dead space of the apparatus. The sample bulb was then cooled to $-196\ ^{\circ}C$ in liquid nitrogen and the level of the liquid nitrogen kept constant. Since the adsorption isotherms were obtained at $-196\ ^{\circ}C$, a correction was made to take account of the effective volume of the apparatus when a part of the system was cooled at this temperature. The corrected plot of the volume versus (temperature/pressure) was a straight line parallel to that obtained at room temperature but having an intercept corresponding to the

Figure 3.3

Count rate of ^{85}Kr Vs pressure



dead space plus the temperature corrected volume. This was verified experimentally when no caesium fluoride was present in the sample bulb.

With the bulb (S) immersed in liquid nitrogen, a second volume versus (temperature/pressure) relationship was determined. The plot obtained was a straight line with the same intercept as the temperature corrected line but with a different gradient. The slope of the latter line was less than that of the corrected line. the differences in volume between the two line corresponded to the amount of ^{85}Kr adsorbed. The number of the molecules adsorbed is given by the equation 3.5. The calculation procedure was as described above and a typical example of this calculation is listed in table 3.7, relevant plots are presented in figures 3.4 and 3.5.

The results obtained for the B.E.T area of caesium fluoride will be discussed in section 3.3.

3.2.3 B.E.T Area Determination of Mercury(II) Fluoride

The B.E.T area of mercury(II) fluoride pretreated with SF_4 and non treated mercury(II) fluoride were determined using ^{85}Kr as adsorbate. The experimental procedure and the methods of calculation were similar to those used with caesium fluoride. The results are presented in section 3.3.

Table 3.7

B.E.T area determination of CsF activated by $(CF_3)_2CO$

Volume cm^3	Count rate count sec^{-1}	Temperature K	Pressure Torr	$T/P \times 10^{-3}$ $K.Torr^{-1}$
103.12	19.87	291.3	0.359	1.120
60.73	29.07	291.6	0.383	0.759
31.20	38.13	291.8	0.519	0.562
20.30	42.74	291.9	0.584	0.499
11.51	48.56	291.4	0.667	0.436
0.00	54.63	290.8	0.753	0.385

Liquid nitrogen temperature

Volume cm^3	Count rate count sec^{-1}	Temperature K	Pressure Torr	$T/P \times 10^{-3}$ $K.Torr^{-1}$
103.12	12.27	292.4	0.152	1.924
60.73	16.48	292.5	0.205	1.425
31.20	20.16	292.8	0.263	1.109
20.30	22.52	292.5	0.297	0.982
11.51	23.91	292.4	0.317	0.921
0.00	27.14	292.4	0.363	0.805

T K	ΔV cm^3	P Torr	$x \times 10^{-18}$	$P_0 - P$ Torr	$\frac{P}{x\ (P_0-P)\times 10^{18}}$	$\frac{P}{P_0}$
294.5	31	0.589	2.288	1.901	0.135	0.236
294.5	57	0.327	2.337	2.163	0.064	0.131
294.5	70	0.267	2.349	2.223	0.051	0.107
294.5	82	0.226	2.328	2.264	0.042	0.090
294.5	95	0.196	2.337	2.294	0.036	0.078

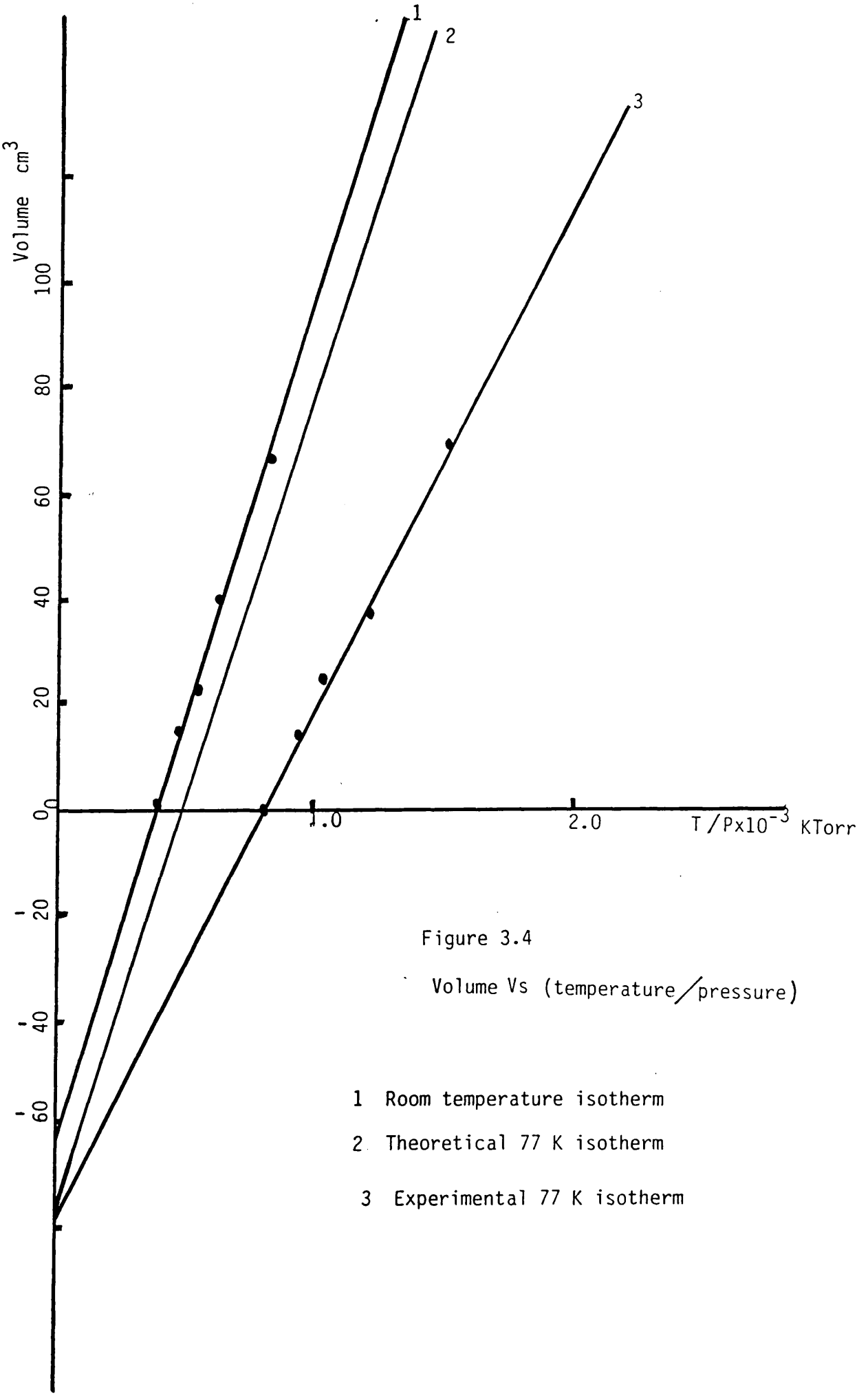


Figure 3.4

Volume Vs (temperature/pressure)

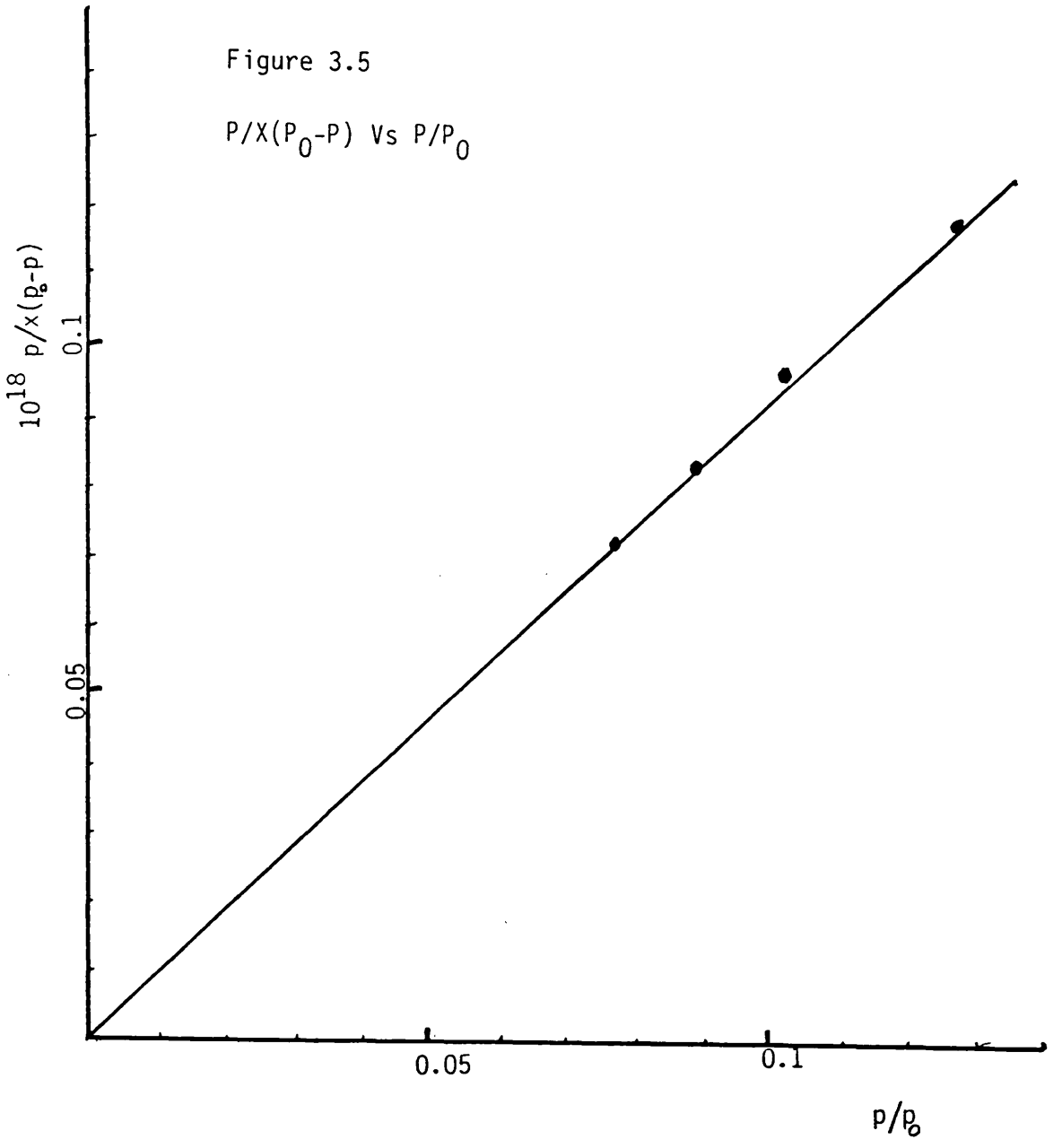
1 Room temperature isotherm

2 Theoretical 77 K isotherm

3 Experimental 77 K isotherm

Figure 3.5

$P/X(P_0-P)$ Vs P/P_0



3.2.4 Determination of the B.E.T Area of Mercury(II) Fluoride Pretreated with Hexafluoroacetone in the Presence of Acetonenitrile

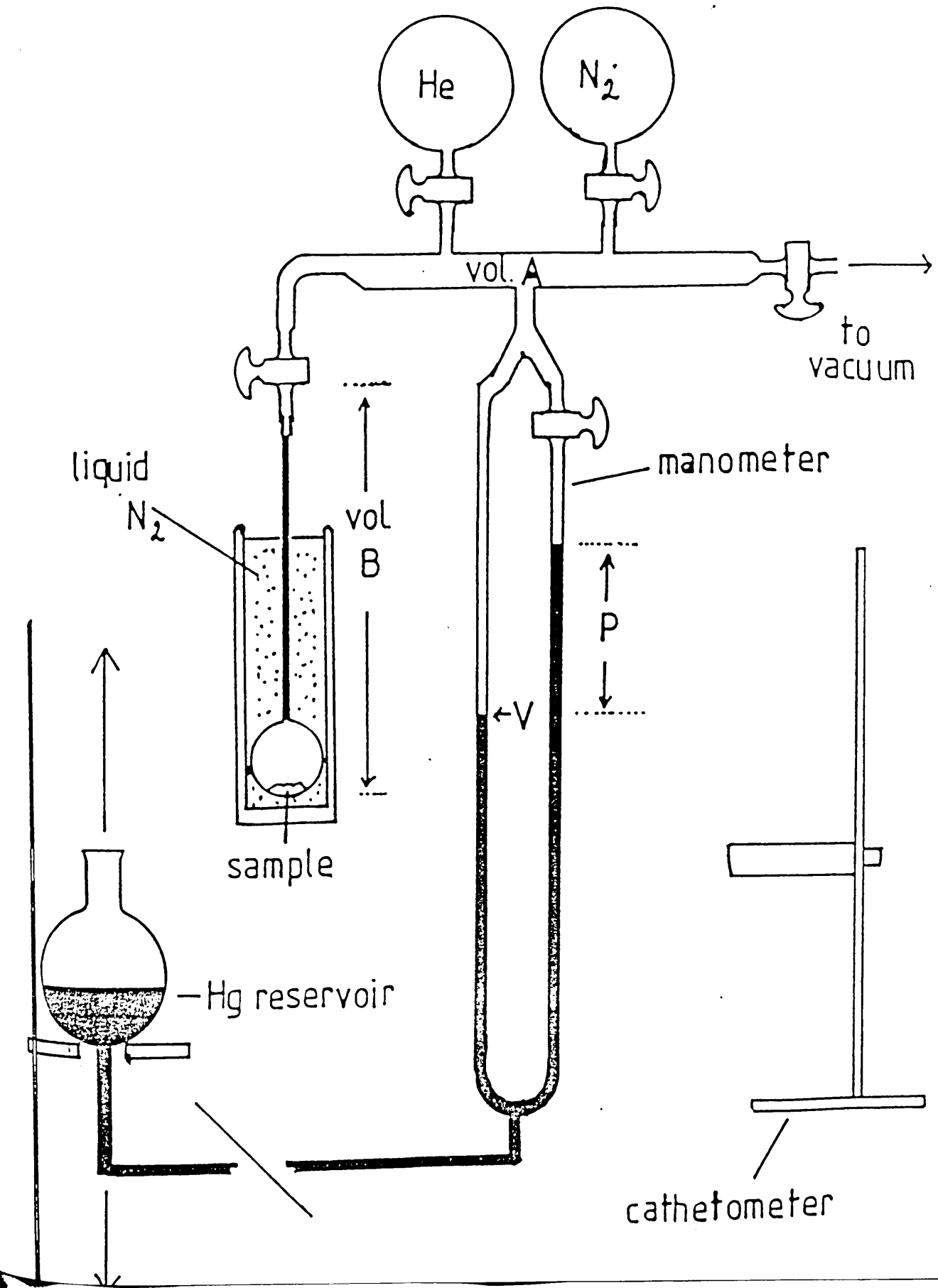
Attempts to use ^{85}Kr were unsuccessful due to the large area of this solid, and hence nitrogen was used as adsorbate for this B.E.T area determination.

The design of the apparatus used is shown diagrammatically in figure 3.6. The adsorbent was placed in a small glass bulb which was attached to the apparatus by mean of standard ground glass joint. Two storage bulbs containing helium and nitrogen were mounted on the manifold, a manometer was also attached to the system. Alteration of the mercury levels in both limbs of the manometer was possible by adjusting the height of the mercury reservoir.

Helium gas was used to determine the dead space of the apparatus and nitrogen was used as adsorbate in the surface area determination. The quantity of nitrogen adsorbed was determined by taking the difference between the measured volume of gas in the manometer and the volume expected on the basis of the gas laws if there had been no adsorbtion. Therefore, it was necessary to determine the dead space comprising sections A and B of the apparatus shown in figure 3.6. These sections were calibrated using helium gas since it was not adsorbed to any appreciable extent at $-196\ ^{\circ}C$. The calibration was carried out by evacuating the system and then admitting helium to section A with section B isolated. A set of readings of volume and pressure was obtained. By the gas laws

Figure 3.6

B E T apparatus



$$(V + A) = \frac{K\ T}{P} \qquad \text{Eq. 3.9}$$

where K = constant whose value depends on the size of helium sample taken

A = dead space above the zero mark on the burette

T = temperature (K)

P = pressure (Torr)

A plot of volume against (temperature/pressure) had slope K and intercept $(-A)$.

Volume B was determined using the same sample of helium but with the sample bulb B, containing mercury(II) fluoride, immersed in liquid nitrogen and open to the rest of the manifold. In this case

$$(V + A + B) = \frac{K\ T}{P} \qquad \text{Eq. 3.10}$$

where B is the effective volume of section B.

In this case, a plot of volume against (temperature/pressure) was a straight line with the same slope as before and intercept equal to $-(A + B)$.

The same procedure was repeated with nitrogen as adsorbate, firstly at room temperature and then at $-196\ ^{o}C$, to give two further plots of volume against (temperature/pressure) with different slopes but with identical intercepts to the corresponding helium determinations. On the basis of the helium adsorption at $-196\ ^{o}C$, the corresponding data for nitrogen resulted in a line parallel to the room temperature isotherm for nitrogen with an

intercept − (A + B). At a given pressure the difference between the volume coordinate on this line and that on the experimental line was the volume adsorbed measured at the apropriate pressure.

The number of molecules adsorbed was calculated from equation 3.5. The procedure for the surface area calculation was identical to that described in section 3.2.2. A typical example of a surface area determination for activated mercury(II) fluoride is presented in table 3.8 and relevant plots of volume against (temperature/pressure) are shown in figure 3.7.

3.3 Results and Discussion

Mercury(II) fluoride was activated in the same way as that used for the activation of caesium fluoride. The reaction of hexafluoroacetone with caesium fluoride to form the heptafluoroisopropoxide was initially reported by Redwood and Willis[93]. The reaction of hexafluoroacetone with mercury(II) fluoride as described above appears not to have been reported in the literature.

A mass balance of the adduct formed before and after decomposition was examined using three different freshly activated samples. The results obtained are summarised in table 3.5. These indicate that the loss of mass of the solid after decomposition was identical to the mass of hexafluoroacetone collected from the decomposition. This mass balance agreed well with hexafluoroacetone being retained as $Hg[(CF_3)_2FCO]_2$.

Table 3.8

B.E.T area determination of HgF_2 activated by $(CF_3)_2CO$

He at room temperature						He at -196°C					
V cm^3	P_1 Torr	P_2 Torr	ΔP Torr	T K	T/P K $Torr^{-1}$	V cm^3	P_1 Torr	P_2 Torr	ΔP Torr	T K	T/P K $Torr^{-1}$
76.1	182.61	318.33	135.72	296.7	2.18	67.1	236.71	317.74	81.03	296.7	3.66
66.8	239.25	394.46	155.21	296.6	1.91	56.6	300.59	383.34	87.75	296.6	3.58
57.9	292.62	417.11	178.49	296.6	1.66	46.6	361.48	456.69	95.21	296.6	3.11
50.2	339.13	543.16	204.03	296.7	1.45	38.5	410.30	512.85	102.55	296.5	2.89
42.9	383.18	619.42	236.24	296.7	1.25	27.1	479.35	594.14	114.84	296.5	2.58

N_2 at room temperature						N_2 at -196°C					
V cm^3	P_1 Torr	P_2 Torr	ΔP Torr	T K	T/P K $Torr^{-1}$	V cm^3	P_1 Torr	P_2 Torr	ΔP Torr	T K	T/P K $Torr^{-1}$
80.2	157.12	342.08	184.96	296.6	1.60	74.7	190.99	297.22	106.23	296.7	2.79
72.1	206.19	412.47	206.28	296.7	1.43	65.7	244.27	357.95	113.68	296.7	2.60
62.9	262.00	497.47	235.47	296.7	1.26	54.8	310.98	434.57	123.59	296.6	2.39
57.5	295.08	552.79	257.71	296.6	1.15	46.9	359.08	490.75	131.67	296.6	2.25
51.1	333.76	621.10	287.34	296.7	1.03	33.0	443.41	593.42	150.01	296.6	1.97

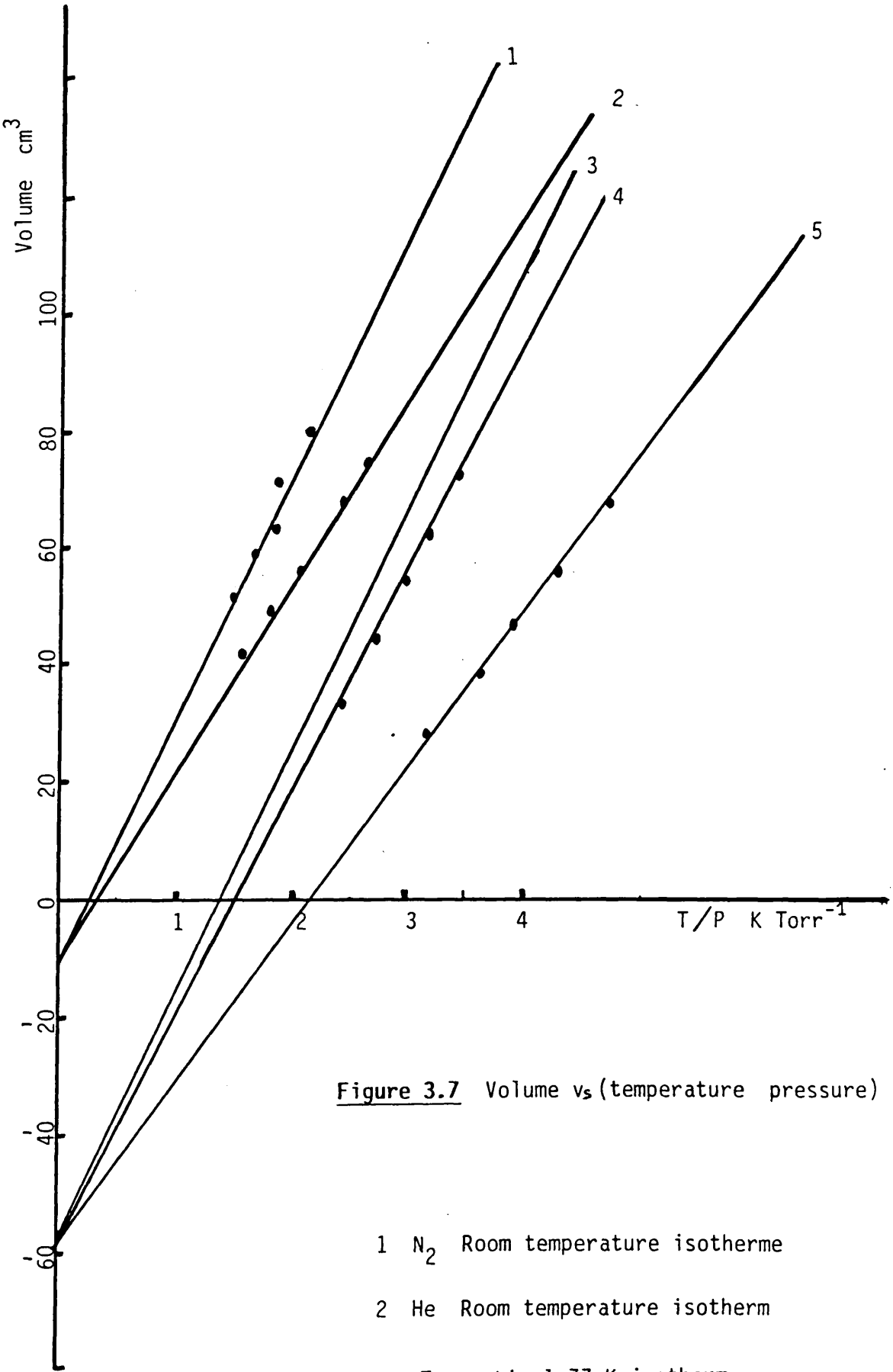


Figure 3.7 Volume vs (temperature pressure)

1 N_2 Room temperature isotherme

2 He Room temperature isotherm

3 Theoretical 77 K isotherm

4 He 77 K isotherm

5 N_2 77 K isotherm

The infrared study of the adduct formed with caesium fluoride, stated that the band at 1510 cm^{-1} is assigned to C–O stretching bond by analogy with that present in the ions CO_3^{-2} (1410 – 1450 cm^{-1}), $HCOO^-$ and CH_3COO^- (near 1570 cm^{-1}), and CF_3COO^- (1700 cm^{-1})[93]. This band is shifted by approximtely 300 cm^{-1} wave number, consistent with change from a CO double bond to a CO single bond.

With mercury(ll) fluoride, the infrared spectrum of the adduct formed table 3.3 showed the presence of eight bands. The CO frequency in the hexafluoroacetone is shifted by 100 cm^{-1}wave number in the adduct formed. Although the thermal decomposition of the adduct formed with mercury(II) fluoride was carried out for only 12h, at a temperature (80 °C) less than that of caesium fluoride (120 °C),unlike caesium fluoride, the infrared spectrum of the solid remaining after the thermal decomposition indicated no band present attributed to the adduct formed. The gas liberated from the decomposition had the same bands as authentic hexafluoroacetone suggesting that the bands obtained with the solid before the thermal decompsition was due to the retention of hexafluoroacetone.

The pretreatment of mercury(II) fluoride with sulphur tetrafluoride led to the formation of thionyl fluoride and silicon tetrafluoride, table 3.6. The latter is believed to be formed from the reaction of hydrogen fluoride and the Pyrex glassware. This formation of hydrogen fluoride and thionyl fluoride is more likely due to the partial hydrolysis of sulphur tetrafluoride by water present on the surface of mercury(II) fluoride. However, the change in the colour of mercury(II) fluoride from yellow to white when treated with sulphur tetrafluoride is due to the removal of this water.

Surface areas on different samples were determined using the appropriate adsorbate ^{85}Kr or N_2. In this B.E.T area determination, the error was calculated by determining an interval within which it is highly probable that the true value lies. This interval is called the reliability interval and the probability selected is called the reliability coefficient, the reliability interval is given by the equation.

$$L_{1,2} = \bar{X} \pm K_n R \qquad \text{Eq. 3.11}$$

where L_1 = the lower limit of the reliability interval

L_2 = the upper limit of the reliability interval

$\bar{X}$ = the mean value.

R = the range of the results.

Kn = the reliability coefficient[100]

In all B.E.T area determinations, the reliability intervals in which the true value lies, were calculated with a probability of 95%.

The B.E.T areas of hexafluoroacetone activated caesium fluoride presented in table 3.9 were obtained on three different samples. By applying equation 3.11 to these results, the reliability interval in which the true value lies with a probability of 95% is 1.83——2.45 m^2g^{-1}.

In the case of mercury(II) fluoride, untreated, pretreated with sulphur tetrafluoride and mercury(II) fluoride pretreated with

hexafluoroacetone in the presence of acetonitrile were examined.

Six B.E.T area determinations were carried out, two on each of three different samples of non treated mercury(II) fluoride. The range of the results are listed in table 3.10, from which it can be deduced that the true value lies, with a probability of 95%, in the range 0.70—1.32 m^2g^{-1}.

Table 3.11 shows the results of six surface area determinations of sulphur tetrafluoride pretreated mercury(II) fluoride. The true value calculated from equation 3.11 is in the range 1.72—2.40 m^2g^{-1}.

Due to the large surface area expected for mercury(II) fluoride pretreated with hexafluoroacetone in the presence of acetonitrile, nitrogen was used as adsorbate. Six B.E.T area determinations were obtained on three freshly activated samples. The results are shown in table 3.12 and the true value of these results lies in the interval 16.26—20.94 m^2g^{-1}.

It appears from the results shown previously that a remarkable increase in the B.E.T area of mercury(II) fluoride was obtained by treatment with hexafluoroacetone, followed by thermal decomposition of the adduct formed. The increase in the surface area can be obtained by the removal of parts of a parent solid in such manner as to leave pores. The walls of these pores comprise the surface area of the resultant solid. A large surface area can be also obtained by the thermal decomposition of the type.

Table 3.9

B E T area of CsF activated by $(CF_3)_2CO$

Run	Batch	Sample	B E T area m^2g^{-1}
1	1	1	1.79
2	1	1	2.23
3	2	1	2.35
4	2	1	1.95
5	2	1	2.41
6	2	2	2.15

Table 3.10

B E T area of HgF_2

Run	Batch	Sample	B E T area m^2g^{-1}
1	1	1	0.71
2	1	1	0.82
3	1	2	1.18
4	1	2	0.96
5	1	3	1.32
6	1	3	1.11

Table 3.11

B E T area of HgF_2 pretreated with SF_4

Run	Batch	Sample	B E T area m^2g^{-1}
1	1	1	1.75
2	1	1	2.14
3	2	1	2.42
4	2	1	1.96
5	3	1	2.21
6	3	2	1.89

Table 3.12

B E T area of HgF_2 activated by $(CF_3)_2CO$

Run	Batch	Sample	B E T area m^2g^{-1}
1	1	1	16.43
2	1	1	18.76
3	2	1	18.48
4	2	2	17.64
5	3	1	19.22
6	3	2	20.13

$$A_{(s)} \longrightarrow B_{(s)} + C_{(g)}$$

This type of decomposition is known to produce a reduction in the particle sizes, and correspondingly, an increase in the surface area[101].

The increase of the B.E.T area of mercury(II) fluoride activated by hexafluoroacetone in the presence of acetonitrile is less likely to be due to the decrease in the particle size, than to formation of the porous solid structure, which is highly probable. A microporeous structure is likely to be involved, since the pretreatment process greatly enhanced the adsorption potential.

The pore systems of a solid are of many different kinds. They may vary greatly both in size and in shape within a given solid as between one solid and another. A convenient classification of pores according to their width has been proposed by Dubinin[102]. Pores of width below 20 Å are described as micropores, those with width above 200 Å are macropores and those with width between 20 and 200 Å are termed transitional pores.

The adsorption potential is significantly higher in the micropores resulting from the overlap of the field of opposite walls of the pores. The amount adsorbed at a given relative pressure is correspondingly enhanced. In a large pore in which the fields of the opposite side of the pores do not overlap, the interaction energy of the solid with the gas molecule is relatively small.

CHAPTER FOUR

CHAPTER FOUR

Reactions of the Probe Molecules Chlorine Monofluoride and Sulphur Tetrafluoride with Mercury(II) Fluoride

Introduction

The ability of ionic metal fluorides such as mercury(II) fluoride to undergo exchange with sulphur tetrafluoride was reported in previous work as the result of a radiotracer study using $[^{18}F]$- fluorine labelled sulphur tetrafluoride[103]. Sulphur tetrafluoride also behaves as a Lewis acid when reacted under heterogeneous conditions with alkali metal fluorides[27]. The ability of these metal fluorides to undergo exchange with $[^{18}F]$- fluorine labelled sulphur tetrafluoride was reported to be in the order.

$$Cs > Rb > K > Na > Li^{(104)}$$

which is consistent with the order of their catalytic activities in synthetic work[104].

Similar Lewis base behaviour of the alkali metal fluorides has been reported in their reactions with chlorine monofluoride, forming complexes of the type $M^+ ClF_2^-$[38]. However, according to Mews[73] chlorine monofluoride apparently does not react with mercury(II) fluoride at room temperature. Since the Lewis acid- base reaction between chlorine monofluoride and caesium fluoride results in poisoning of the catalyst[72], the lack of reaction between mercury(II) fluoride and chlorine

monofluoride, if confirmed, would be a distinct advantage in the synthesis of sulphur chloride pentafluoride from chlorine monofluoride and sulphur tetrafluoride. The work described below was undertaken to examine the interaction of the probe molecules chlorine monofluoride and sulphur tetrafluoride with mercury(II) fluoride. Using the radiochemically labelled species [^{35}S]– sulphur tetrafluoride and [^{36}Cl]– chlorine labelled chlorine monofluoride, possible poisoning reactions were examined by studying the chemisorption and retention of these molecules at mercury(II) fluoride surfaces, activated as described in chapter 3 by using hexafluoroacetone and sulphur tetrafluoride.

4.1 Experimental

Experiments in which non–radioactive material was used were performed in a Monel metal line described in section 2.1.1(b). Experiments involving the use of the radiochemically labelled species [^{36}Cl]– chlorine labelled chlorine monofluoride and [^{35}S]– sulphur labelled sulphur tetrafluoride were carried out in a Pyrex glass system described in section 2.1.1(a). The reaction vessel (234 cm^3) shown in figure 2.4 was equipped with two Geiger Müller counters intercalibrated as described in section 2.4.7.

Plots of pressure versus count rate for each of the labelled gases used in this work were constructed. Linear relationships were found in each case. Typical examples of these calibrations are listed in tables 4.1 and 4.2 and are shown in figures 4.1 and 4.2. The stoichiometries of the uptakes of chlorine monofluoride and sulphur tetrafluoride by mercury(II) fluoride

Table 4.1

Variation of count rate versus pressure of [^{36}Cl]-ClF

Geiger Müller 1 count corrected for background	GM1 count rate count min^{-1}	Geiger Müller 2 count corrected for background	GM2 count rate count min^{-1}	Presure Torr
2511 ± 50	251 ± 5	2564 ± 51	256 ± 5	10 ± 1
4325 ± 66	432 ± 7	4407 ± 66	441 ± 7	15 ± 1
7226 ± 85	723 ± 9	8035 ± 89	803 ± 9	25 ± 1
10214 ± 101	1023 ± 10	10226 ± 101	1022 ± 10	33 ± 1
12467 ± 111	1247 ± 11	12526 ± 112	1253 ± 11	42 ± 1
15758 ± 125	1575 ± 12	15684 ± 125	1568 ± 12	50 ± 1
19023 ± 138	1902 ± 14	19115 ± 138	1911 ± 14	60 ± 1
22064 ± 148	2206 ± 15	21993 ± 148	2199 ± 15	70 ± 1
25982 ± 168	2598 ± 16	26015 ± 168	2601 ± 16	80 ± 1

Inter calibration factor = 1.05

Counting time = 10 min

Table 4.2

Variation of count rate versus pressure of [^{35}S]-SF_4

Geiger müller 1 count corrected for background	GM1 count rate count min^{-1}	Geiger Müller 2 count corrected for background	GM2 count rate count min^{-1}	Pressure Torr
5730 ± 76	573 ± 8	5658 ± 75	566 ± 7	10 ± 0.5
12438 ± 111	1244 ± 11	12675 ± 120	1267 ± 12	20 ± 0.5
18601 ± 136	1860 ± 14	18432 ± 136	1843 ± 14	30 ± 0.5
24024 ± 155	2402 ± 15	23736 ± 154	2374 ± 15	40 ± 0.5
30162 ± 174	3016 ± 17	29262 ± 171	2926 ± 17	50 ± 0.5
36246 ± 190	3624 ± 19	35544 ± 188	3554 ± 19	60 ± 0.5
40476 ± 201	4047 ± 20	38988 ± 197	3899 ± 20	70 ± 0.5
44928 ± 212	4493 ± 21	44076 ± 210	4408 ± 21	80 ± 0.5

Inter calibration factor = 1.02

Counting time = 10 min

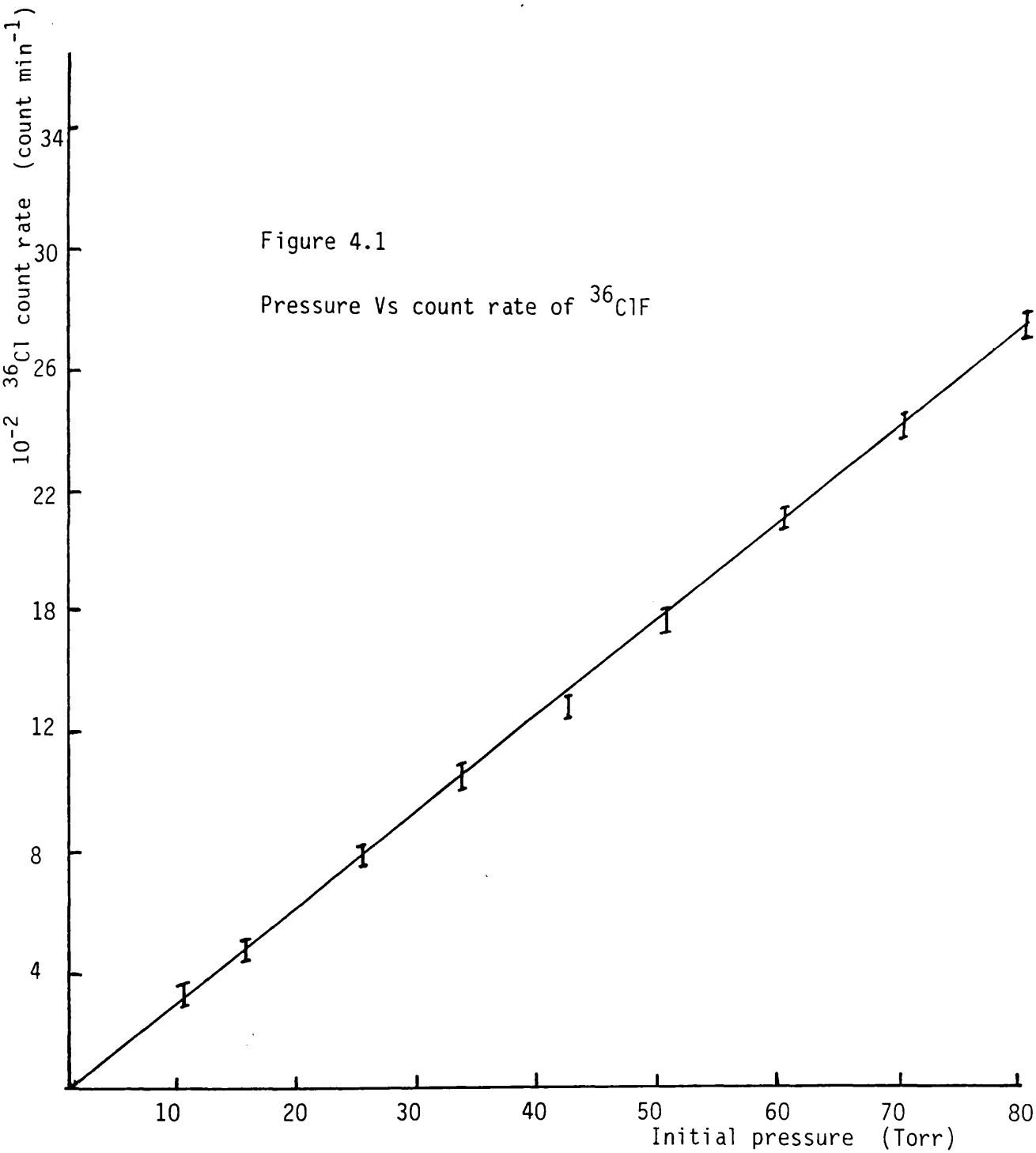
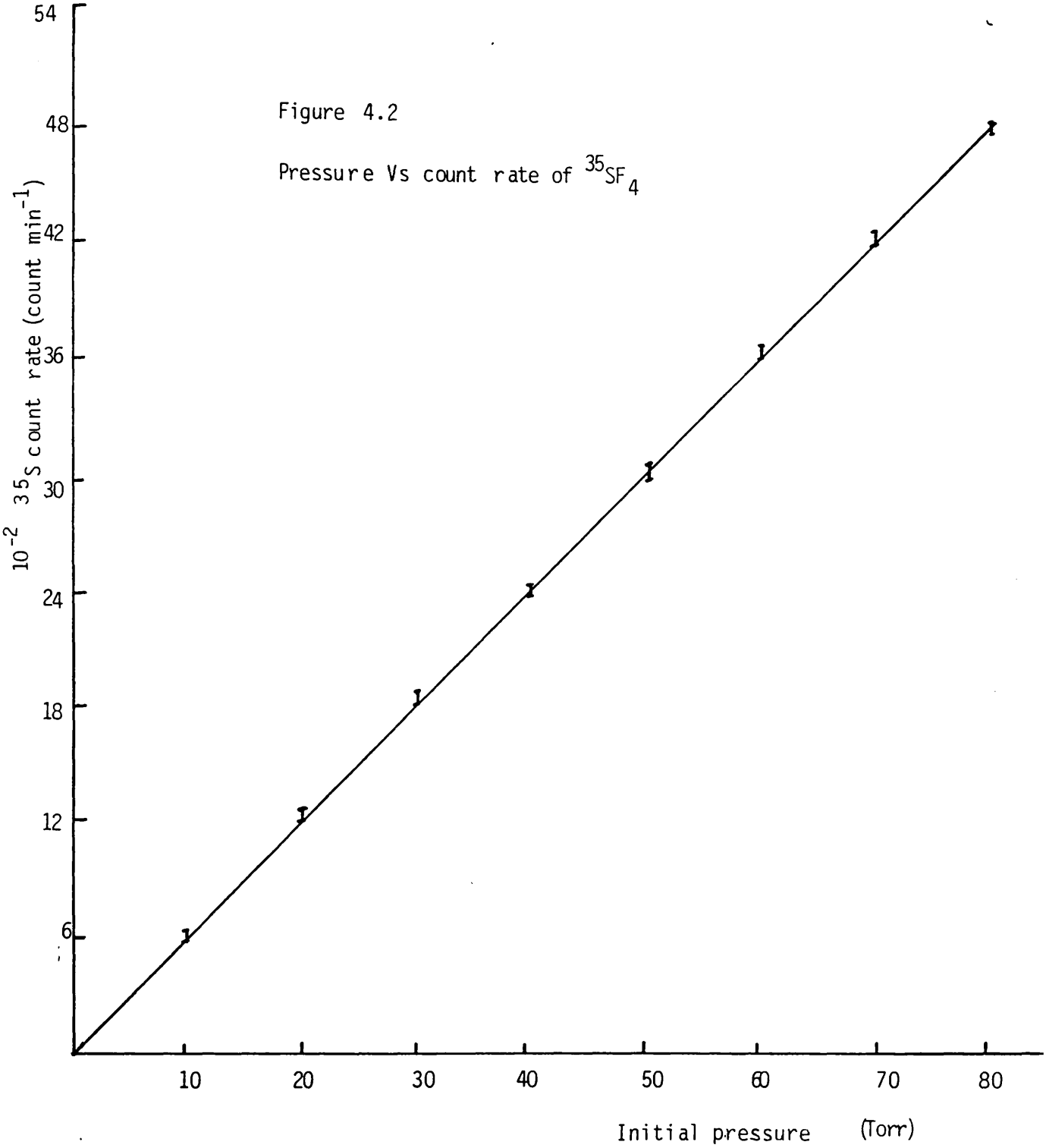


Figure 4.1

Pressure Vs count rate of ^{36}ClF

Figure 4.2

Pressure Vs count rate of $^{35}SF_4$



were determined using these calibration relationships. The drop in the gas phase count rate when the gas reacted with the solid was converted to pressure using the expression.

$$P = C_{cps} \cdot S \qquad \text{Eq. 4.1}$$

where P = pressure (Torr), C_{cps} = count rate (count sec^{-1}) and S = slope of the plot of count rate versus pressure.

Mercury(II) fluoride (untreated and treated with hexafluoroacetone or sulphur tetrafluoride) was handled in an inert atmosphere box. A weighed amount (1.5–3.0 g, 6.3–12.6 mmol) was ground in an agate mortar and pestle. The sample was placed in an ampoule and the stopcock was closed. The vessel was transferred to the vacuum line where it was evacuated for 0.5 h. After closing the stopcock, the ampoule was mounted on the counting vessel via a B 14 socket. The system was pumped out and subsequently isolated from the pump. A known quantity of the relevant radiochemically labelled gas was admitted into the reaction vessel. [^{36}S]– Sulphur labelled sulphur tetrafluoride was directly expanded into the reaction vessel from a storage Monel metal pressure vessel. In the case of [^{36}Cl]– chlorine labelled chlorine monofluoride, the gas measurements were carried out in the Monel metal line, where a known quantity of gas was condensed in a Monel metal pressure vessel (87 cm^3). Subsequently this vessel was connected to the Pyrex glass system, the labelled gas was then admitted to the reaction vessel from the Monel metal pressure vessel taking into account the change in volume, and the count rate was determined.

This corresponded to the count rate of the gas before reaction. The gas was then removed from the reaction vessel and stored in the gas handling manifold.

The ampoule containing mercury(II) fluoride was opened to allow the sample to fall into one of the sections of the movable glass boat. The stopcock on the ampoule was closed and the section of the boat containing mercury(II) fluoride was positioned directly under one of the Geiger Müller tubes. The radiochemically labelled gas was readmitted into the reaction vessel. Geiger Müller tube (1) monitored the radioactivity in the gas phase and Geiger Müller (2) monitored the radioactivity on the solid and in the gas phase, therefore the surface solid count rate could be obtained by a simple subtraction of the intercalibrated count rates. A typical set of data obtained for [^{36}Cl]- chlorine labelled chlorine monofluoride reacting with mercury(II) fluoride, activated by hexafluoroacetone, is given in table 4.3.

4.2 Results of the Reaction of Chlorine Monofluoride with Mercury(II) Fluoride

4.2.1 Reaction of Chloride Monofluoride with Mercury(II) Fluoride Activated by Hexafluoroacetone

The reaction between chlorine monofluoride and mercury(II) fluoride, activated by hexafluoroacetone as described in section 3.1.2, was studied using [^{36}Cl]- chlorine labelled chlorine monofluoride and by conventional manometric methods.

Table 4.3

Reaction of [^{36}Cl]-ClF with HgF_2 activated by $(CF_3)_2CO$

Variation of count rate with time

Initial pressure = 50Torr

Sample weight = 3.0 g

Time	GM1 Gas only corrected for background	GM2 Gas+Solid corrected for background	GM1 count rate	GM2 count rate	Surface count rate
min	cout	count	count min^{-1}	count min^{-1}	cout min^{-1}
05	4142 ± 64	118613 ± 344	414 ± 6	11861 ± 34	11447 ± 41
15	3817 ± 61	120319 ± 347	382 ± 6	12031 ± 35	11650 ± 41
25	3609 ± 60	120631 ± 347	361 ± 6	12063 ± 35	11702 ± 41
35	3727 ± 61	120444 ± 347	372 ± 6	12044 ± 35	11671 ± 41
45	3684 ± 60	120435 ± 347	368 ± 6	12043 ± 35	11676 ± 41
55	3557 ± 59	120673 ± 347	356 ± 6	12067 ± 35	11711 ± 41
65	3468 ± 59	120897 ± 347	347 ± 6	12089 ± 35	11742 ± 41

counting time = 600 S

The admission of [^{36}Cl]– chlorine labelled chlorine monofluoride (50 Torr) to a sample of mercury(II) fluoride (3.0 g, 12.6 mmol), activated as described, resulted in an immediate constant value of the [^{36}Cl]– chlorine count rate at the solid surface. The [^{36}Cl]– chlorine count rate on the surface of the solid was followed over 1 h at room temperature. A plot of surface count rate versus time is presented in figure 4.3. This showed that the surface count rate remained constant. Apparently the reaction was complete with the first measurement.

The variation in the gas phase count rate determined by the second Geiger Müller tube was also followed with time. The gas phase count rate observed due to the gas alone in the reaction vessel decreased sharply when the solid was added. The overall drop in gas count rate, that is the difference between the count rate of gas before reaction and the last point in the reaction, gave a measure of the total uptake of the gas by the solid. The uptake of [^{36}Cl]– chlorine labelled chlorine monofluoride by the solid was calculated from this drop in the gas phase count rate and was found to be 0.47 mmol.

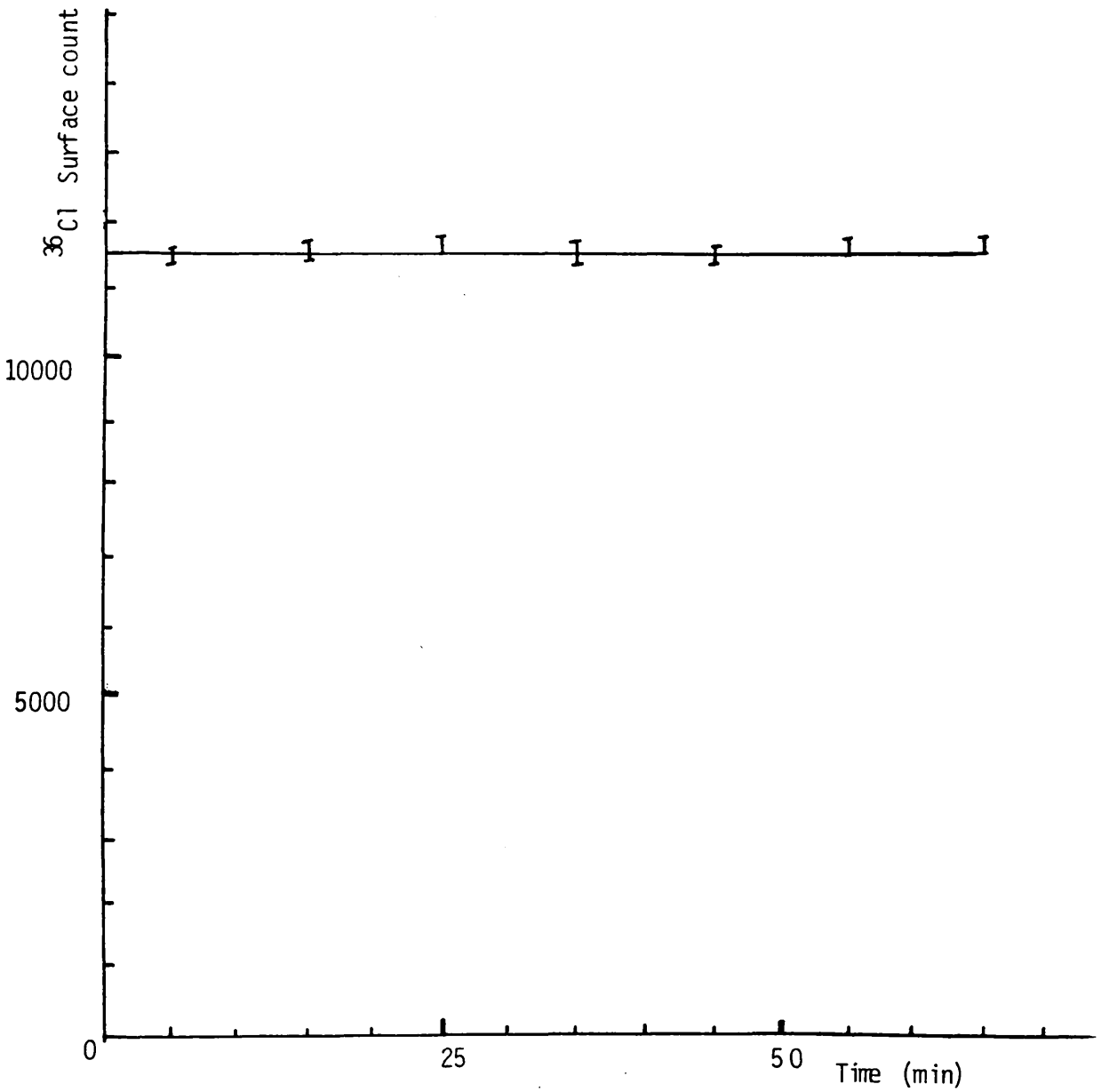
After 1 h of reaction, the volatile material was removed at room temperature by distillation and the solid subsequently pumped. The variation of the [^{36}Cl]– chlorine surface count rate was followed with time during the evacuation process. A decrease in the surface count rate was observed, although the process was very slow. The surface count rate decreased over a 4 h period of evacuation at room temperature from 11700 to a value of ca 7500 count min^{-1}. This indicated that the [^{36}Cl]– chlorine count rate at the solid surface remained very high and that only 35% of the surface

Figure 4.3

Reaction of ^{36}ClF with HgF_2 activated by $(CF_3)_2CO$

Variation of ^{36}Cl surface count rate with time

Sample weight = 3.0 g



Counting time = 10 min

The points are set at the mean time of each counting period

Pressure = 50 Torr

[^{36}Cl] activity was removed. Since at this point the surface count rate was still decreasing, the solid was evacuated at room temperature overnight. After 16 h, 45% of the surface activity had been removed and no further decrease was observed. Therefore 55% of the [^{36}Cl]- chlorine surface activity was permanently retained on the surface.

Further admission of an identical quantity of [^{36}Cl]- chlorine labelled chlorine monofluoride to mercury(II) fluoride following the first adsorption- desorption experiment, resulted in a saturation surface count rate which was less than that obtained in the first experiment. Subsequent evacuation of the solid for the same period of time resulted in a count rate from the surface equal to that obtained in the first desorption experiment.

The procedure described above was repeated 3 times using the same pressure of [^{36}Cl]- chlorine labelled chlorine monofluoride. In each experiment a fresh sample of mercury(II) fluoride (3.0 g, 12.6 mmol) activated by hexafluoroacetone was used and similar behaviour was observed. A typical example of the change in the [^{36}Cl]- chlorine surface count rate versus time during the adsorption- desorption process is presented in figure 4.4. Since the desorption process was followed with time for only 4 h and subsequently the solid was left pumping overnight, only the first portions of the first and second desorption processes in figure 4.4 are well defined.

The surface count rate and uptake of [^{36}Cl]- chlorine labelled chlorine monofluoride by the solid versus initial pressure of gas used were

Figure 4.4

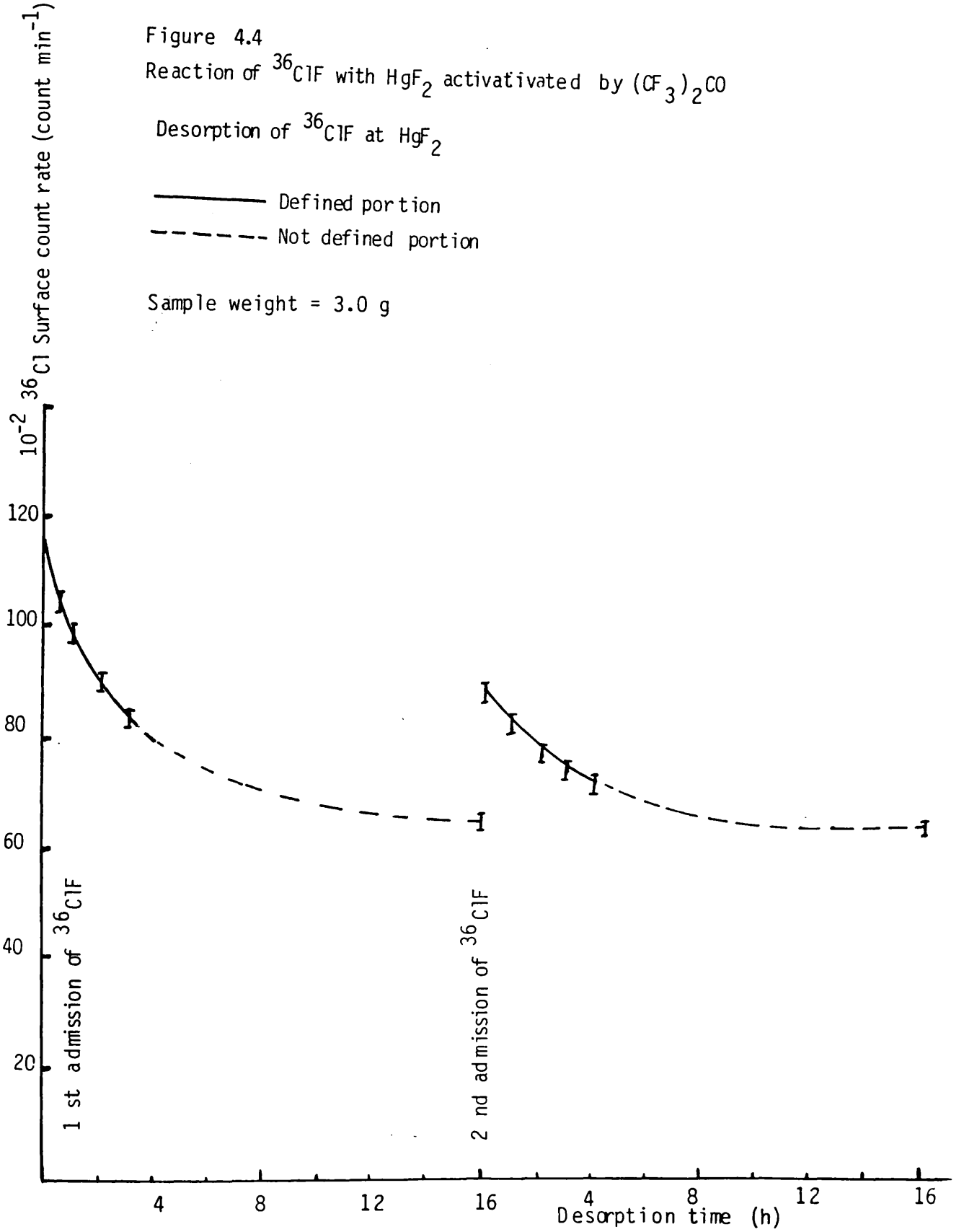
Reaction of ^{36}ClF with HgF_2 activativated by $(CF_3)_2CO$

Desorption of ^{36}ClF at HgF_2

——— Defined portion

– – – – – Not defined portion

Sample weight = 3.0 g



Counting time = 10 min

pressure = 50Torr

studied over the range 10—250 Torr by monitoring the count rate changes of the gas and gas plus surface. In each experiment, a fresh sample of mercury(II) fluoride (1.5 g, 6.3 mmol) activated by hexafluoroacetone was allowed to react with [^{36}Cl]- chlorine labelled chlorine monofluoride at room temperature for 1 h. The surface count rate, recorded after this time of contact, versus initial pressure is presented in figure 4.5. This indicated that the surface count rate over the range 10—70 Torr increased rapidly as the initial pressure increased. Above an initial pressure of 70 Torr, the increase was less marked and it reached a constant value at an initial pressure of 120 Torr. The total uptake of [^{36}Cl]- chlorine labelled chlorine monofluoride by the solid showed very similar behaviour. It increased markedly over the range of 10—70 Torr, thereafter the increases were less marked. The variation of [^{36}Cl]- chlorine labelled chlorine monofluoride solid uptake versus initial pressure is shown schematically in figure 4.6. The uptake of [^{36}Cl]- chlorine labelled chlorine monofluoride by mercury(II) fluoride was independent of pressure at pressures greater than 90 Torr.

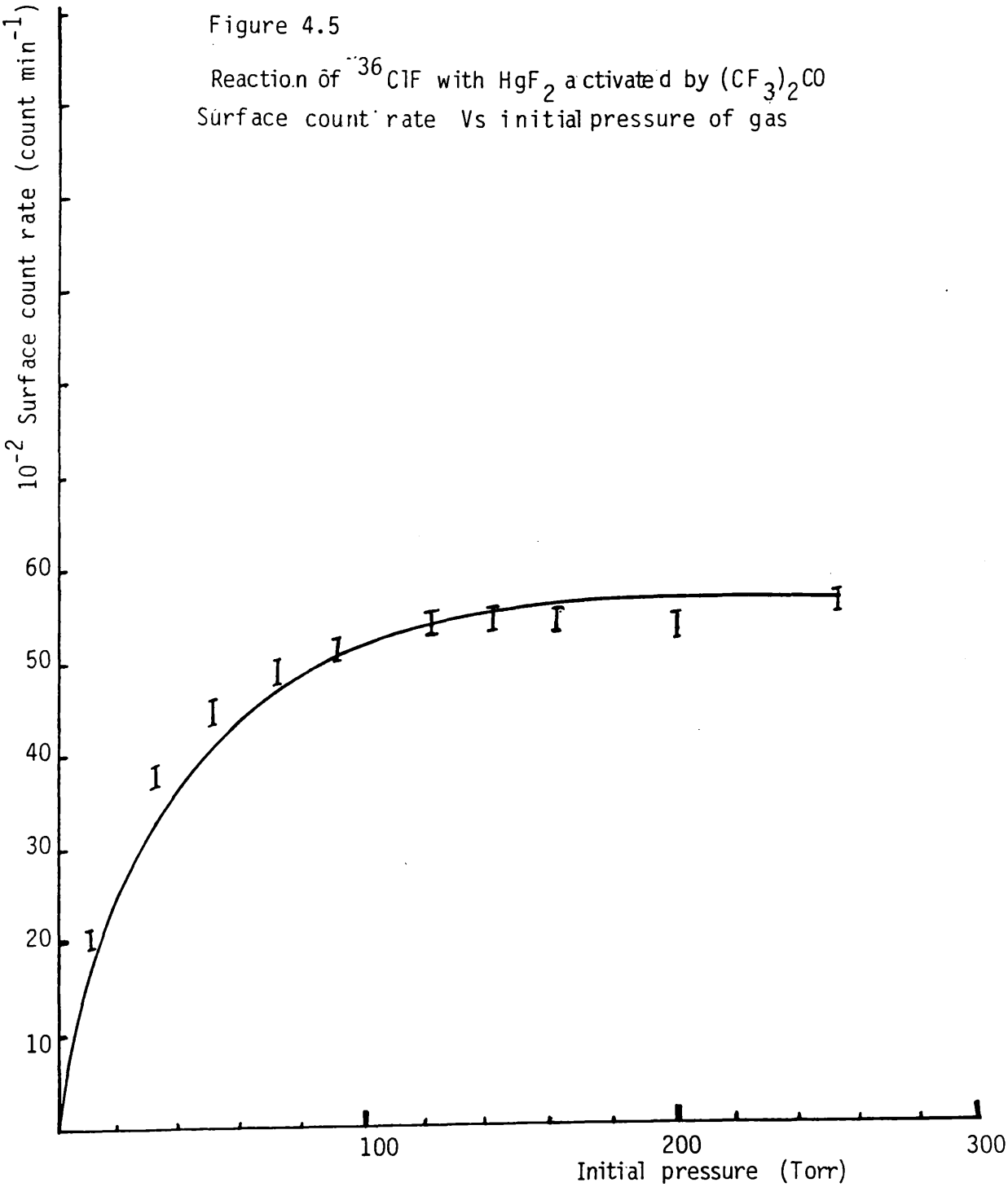
In each experiment, after 1 h of contact of [^{36}Cl]- chlorine labelled chlorine monofluoride with the mercury(II) fluoride at room temperature, the solid was evacuated for 16 h and the count rate of the [^{36}Cl]- chlorine on the surface was determined. The results obtained using different pressures of [^{36}Cl]- chlorine labelled chlorine monofluoride are summarized in table 4.4.

The behaviour of the uptake of chlorine monofluoride by hexafluoroacetone activated mercury(II) fluoride at different initial pressures

Figure 4.5

Reaction of ^{36}ClF with HgF_2 activated by $(CF_3)_2CO$

Surface count rate Vs initial pressure of gas



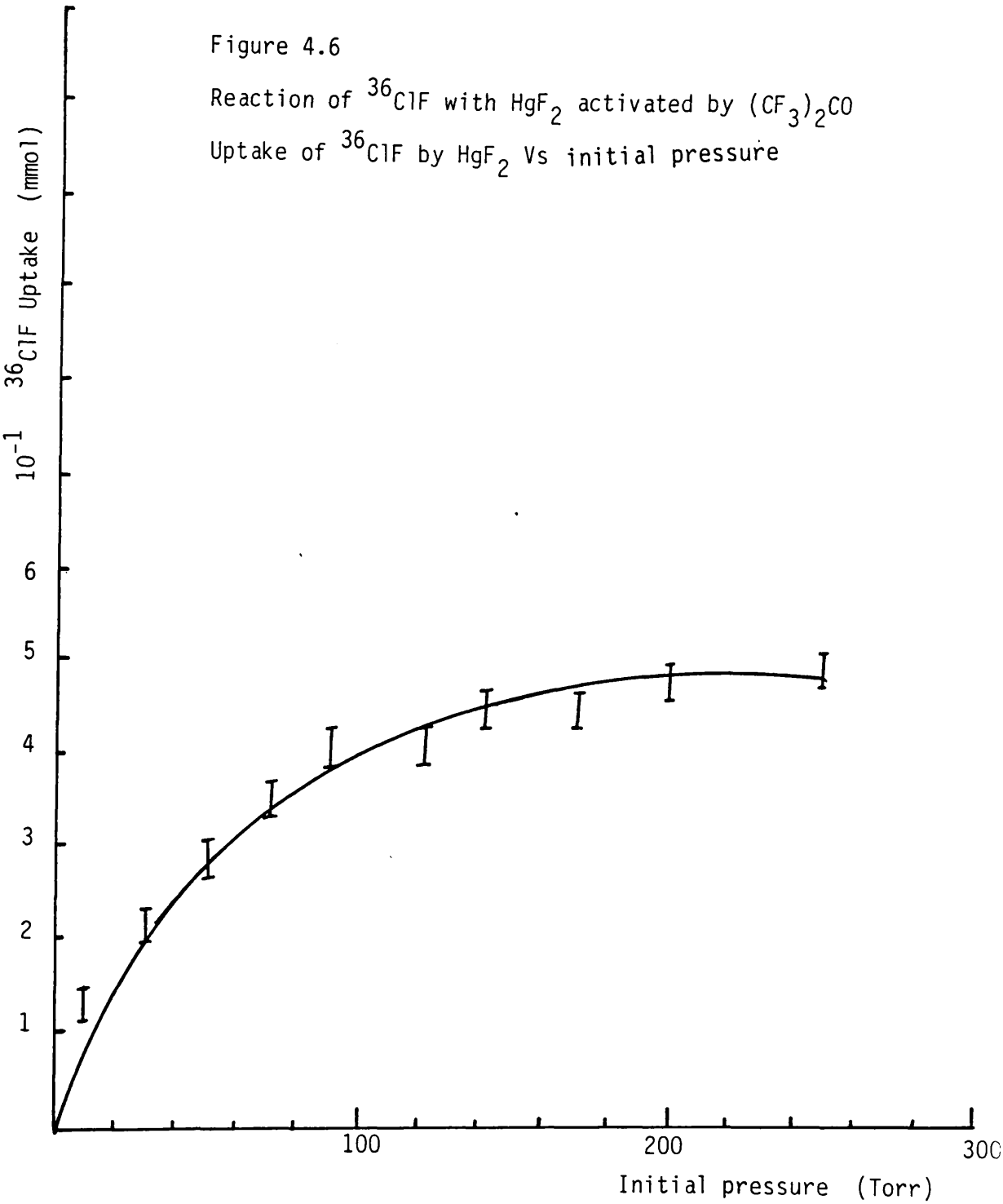
Reaction time = 1 h

Sample weight = 1.5 g

Figure 4.6

Reaction of ^{36}ClF with HgF_2 activated by $(CF_3)_2CO$

Uptake of ^{36}ClF by HgF_2 Vs initial pressure



Reaction time = 1 h

Sample weight = 1.5 g

Table 4.4

Summary of results of reaction of [^{36}Cl]-ClF with HgF_2 activated by $(CF_3)_2CO$

Initial pressure	Total uptake of gas	Solid count rate	Surface count rate after evacation for 16 h
Torr	mmol	count min^{-1}	count mni^{-1}
10 ± 1	0.12 ± 0.002	2216 ± 61	1226 ± 11
30 ± 1	0.19 ± 0.002	3675 ± 61	2043 ± 14
50 ± 1	0.28 ± 0.003	4344 ± 61	2334 ± 15
70 ± 1	0.34 ± 0.004	4899 ± 62	2655 ± 16
90 ± 1	0.42 ± 0.004	4976 ± 62	2791 ± 16
120 ± 1	0.40 ± 0.004	5514 ± 63	3104 ± 17
140 ± 1	0.48 ± 0.004	5525 ± 63	3087 ± 17
170 ± 1	0.41 ± 0.004	5338 ± 63	2878 ± 17
200 ± 1	0.50 ± 0.004	5290 ± 63	2907 ± 17
250 ± 1	0.51 ± 0.004	5479 ± 63	2948 ± 17

Sample weight = 1.5 g

Reaction time = 1 h

was also studied by a conventional manometric method using the Monel metal line described in section 2.1.1 (b). The results obtained are presented in table 4.5. The pattern of the uptake was very similar to that obtained for the [^{36}Cl]- chlorine measurements and the agreement with the uptake calculated from radiochemical methods is good, figure 4.7.

When sulphur tetrafluoride (200 Torr) was admitted to mercury(II) fluoride, previously reacted with [^{36}Cl]- Chlorine labelled chlorine monofluoride, the surface count rate remained unchanged even after allowing sulphur tetrafluoride to react at room temperature for two hours. This experiment was repeated with non labelled species. Mercury(II) fluoride (2.0 g, 8.4 mmol) was allowed to react with chlorine monofluoride (10.0 mmol) in a Monel metal pressure vessel for 2 h at room temperature. The volatile material was then removed by distillation at room temperature and the solid was pumped at room temperature for 16 h. Sulphur tetrafluoride (8.0 mmol) was distilled into the vessel and left to react for 2 h at room temperature. The infrared spectrum of the gas phase after this time of reaction showed no evidence for the presence of sulphur chloride pentafluoride. The small amount of gas trapped at $-80\ c^0$ was identified as sulphur tetrafluoride.

This procedure was repeated four times. In each experiment the reaction time of sulphur tetrafluoride with mercury(II) fluoride pretreated with chlorine monofluoride was extended up to 16 hours, but no evidence for sulphur chloride pentafluoride was obtained.

Table 4.5

The results of the manometric study of the uptake of ClF by HgF_2 activated by $(CF_3)_2CO$

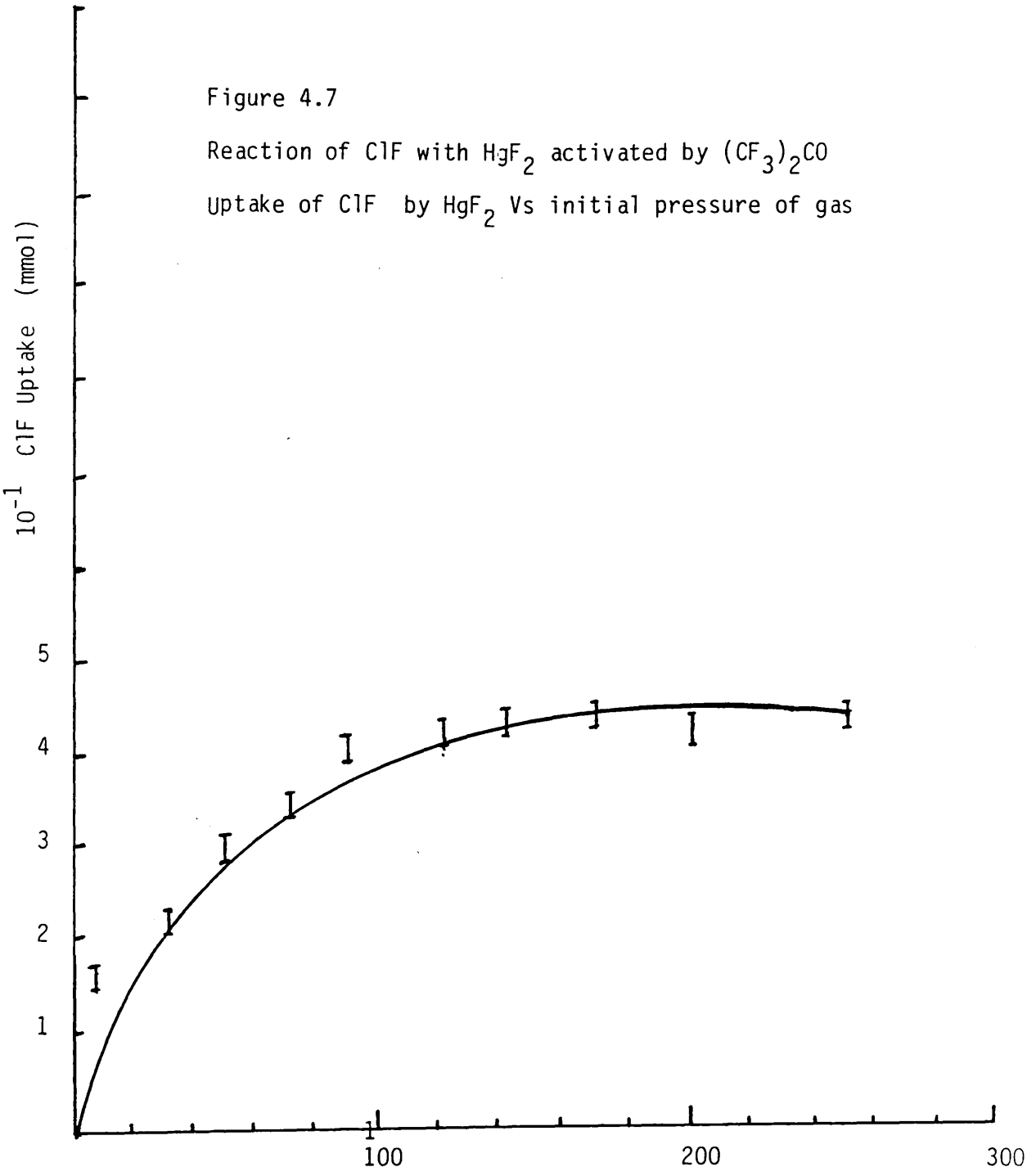
Gas admitted Torr mmol	Fall in pressure Torr	Totaluptake of gas mmol
10 0.12	10 ± 1	0.12 ± 0.01
30 ±1 0.38 ±0.01	16 ± 1	0.20 ± 0.01
50 ± 1 0.65 ±0.01	23 ± 1	0.29 ± 0.01
70 ± 1 0.89 ± 0.01	25 ± 1	0.32 ± 0.01
90 ± 1 1.15 ± 0.01	31 ± 1	0.39 ± 0.01
120 ± 1 1.51 ± 0.01	32 ± 1	0.41 ± 0.01
140 ± 1 1.81 ± 0.01	34 ± 1	0.46 ± 0.01
170 ± 1 2.17 ± 0.01	36 ± 1	0.44 ± 0.01
200 ± 1 2.56 ± 0.01	35 ± 1	0.46 ± 0.01
250 ± 1 3.20 ± 0.01	36 ± 1	

Sample weight = 1.5 g
Reaction time = 1 h

Figure 4.7

Reaction of ClF with HgF_2 activated by $(CF_3)_2CO$

Uptake of ClF by HgF_2 Vs initial pressure of gas



Reaction time = 1 h

Sample weight = 1.5 g

4.2.2 Reaction of Chlorine Monofluoride with Mercury(II) Fluoride Pretreated with Sulphur Tetrafluoride

Mercury(II) fluoride (3.0 g, 12.6 mmol) pretreated with sulphur tetrafluoride, as described in section 4.2.3, was allowed to react at room temperature with [^{36}Cl]- chlorine labelled chlorine monofluoride (50 Torr). The growth of the [^{36}Cl]- chlorine count rate at the solid surface versus time was very slow in comparison with that obtained for mercury(II) fluoride activated by hexafluoroacetone. A plot of surface count rate versus time is presented in figure 4.8. This showed a relatively rapid increase in the [^{36}Cl]- chlorine surface count rate over the first 30 minutes followed, thereafter, by a relatively slow process.

The removal of [^{36}Cl]- chlorine activity at the solid surface by evacuation at room temperature resulted in behaviour similar to that obtained with mercury(II) fluoride activated via hexafluoroacetone. The decrease in the surface count rate was very slow and only 45% of solid activity could be removed after evacuation at room temperature for 16 h.

The surface count rate and uptake of [^{36}Cl]- chlorine labelled chlorine monofluoride by the solid were determined using diffent pressures of gas (10- 200 Torr). A fresh sample of mercury(II) fluoride (1.5 g, 6.3 mmol) was used in each experiment. The behaviour of the [^{36}Cl]- chlorine uptake by solid mercury(II) fluoride pretreated with sulphur tetrafluoride was similar to that of hexafluoroacetone activated mercury(II) fluoride, although the quantities involved with the former were

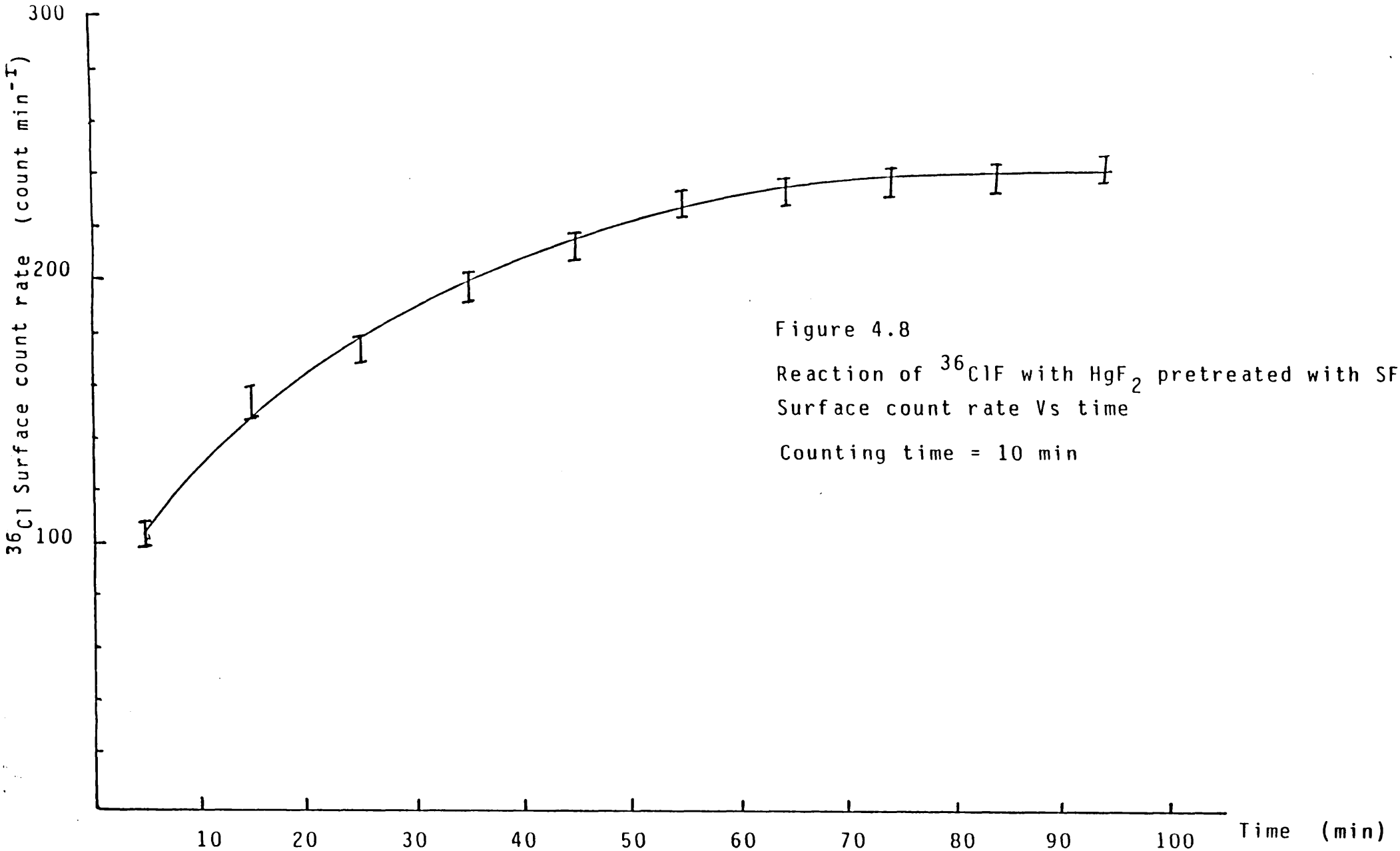


Figure 4.8

Reaction of ^{36}ClF with HgF_2 pretreated with SF_4

Surface count rate Vs time

Counting time = 10 min

much lower in comparison with the latter. The relationship between the surface count rate, recorded after 1.5 h of reaction at room temperature, and the initial pressure is presented in figure 4.9. A surface count rate independent of the initial pressure was observed at pressures greater than 90 Torr. The variation of the uptake of gas by the solid versus initial pressure presented in figure 4.10 showed that the uptake was independent of the initial pressure above 70 Torr. A summary of the results obtained with mercury(II) fluoride pretreated with sulphur tetrafluoride is given in table 4.6.

Since a very small uptake of $[^{36}Cl]$- chlorine labelled chlorine monofluoride was obtained with mercury(II) fluoride pretreated with sulphur tetrafluoride, the study was restricted to radiotracer experiments as conventional manometric measurements were not reliable.

4.3 Reaction of Sulphur Tetrafluoride with Mercury(II) Fluoride

The room temperature reaction between sulphur tetrafluoride and mercury(II) fluoride was studied using $[^{35}S]$- sulphur labelled sulphur tetrafluoride. All reactions between $[^{35}S]$- sulphur labelled sulphur tetrafluoride and mercury(II) fluoride were restricted to mercury(II) fluoride activated via hexafluoroacetone since a very small uptake, not easily quantified, was observed with mercury(II) fluoride pretreated with sulphur tetrafluoride.

The $[^{35}S]$- sulphur surface count rate versus time observed on the

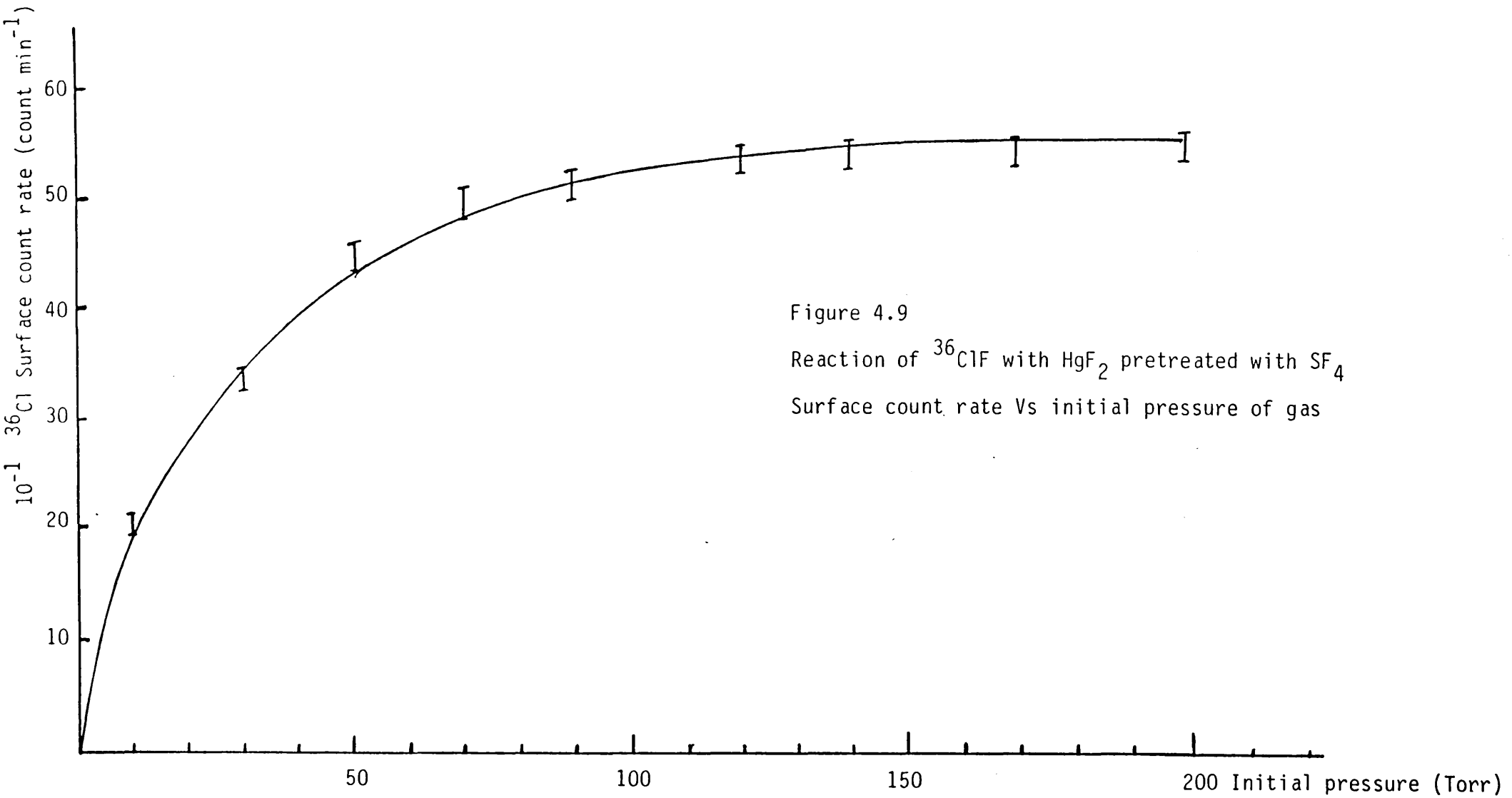


Figure 4.9

Reaction of ^{36}ClF with HgF_2 pretreated with SF_4

Surface count rate Vs initial pressure of gas

Reaction time = 1.5 h

Sample weight = 1.5 g

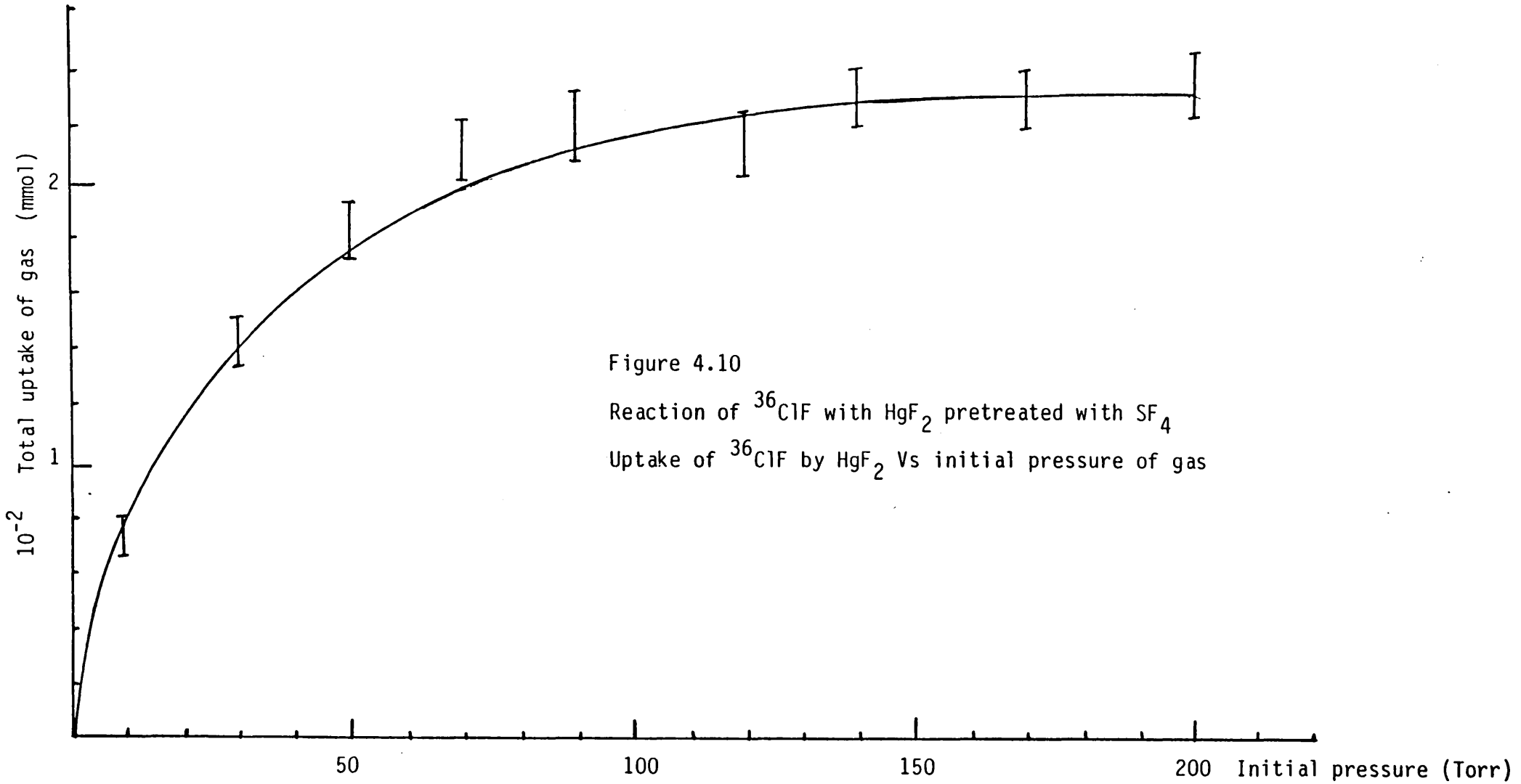


Figure 4.10

Reaction of ^{36}ClF with HgF_2 pretreated with SF_4

Uptake of ^{36}ClF by HgF_2 Vs initial pressure of gas

Reaction time = 1.5 h

Sample weight = 1.5 g

Table 4.6

Summary of results of reaction between [^{36}Cl]-ClF and HgF_2 pretreated with SF_4

Inital prssure Torr	Total uptake of gas mmol	Surface cont rate count min^{-1}
10 ± 1	0.007 ± 0.0005	211 ± 18
30 ± 1	0.014 ± 0.0007	342 ± 18
50 ± 1	0.018 ± 0.0010	456 ± 19
70 ± 1	0.021 ± 0.0010	497 ± 19
90 ± 1	0.022 ± 0.0010	523 ± 19
120 ± 1	0.020 ± 0.0010	519 ± 19
140 ± 1	0.023 ± 0.0010	546 ± 19
170 ± 1	0.023 ± 0.0010	537 ± 19
200 ± 1	0.024 ± 0.0010	541 ± 19

Sample weight = 1.5 g

Reaction time = 1.5 h

surface of the solid when [^{35}S]– sulphur labelled sulphur tetrafluoride was admitted to mercury(II) fluoride activated by hexafluoroacetone, was similar in form to that of [^{36}Cl]– chlorine labelled chlorine monofluoride, the surface count rate achieved after 1.5 h of reaction at room temperature was very low in comparison with that obtained in the reaction between mercury(II) fluoride and [^{36}Cl]– chlorine labelled chlorine monofluoride. Admission of [^{35}S]– sulphur labelled sulphur tetrafluoride (50 Torr) to mercury(II) fluoride (3.0 g, 12.6 mmol) resulted in very rapid increase in the [^{35}S]– sulphur surface count rate and a constant value was obtained from the first measurement.

After 1.5 h of reaction at room temperature the material in the gas phase was removed. Unlike the behaviour of the [^{36}Cl]– chlorine surface count rate, the decrease in [^{35}S]– sulphur surface count rate during the evacuation was very rapid over the first 10 minutes, thereafter remaining almost constant. After 10 minutes of evacuation, 85% of the surface activity was removed and no further decrease occured thereafter.

Further admission of [^{35}S]– sulphur labelled sulphur tetrafluoride after the first adsorption/desorption cycle led to a saturation surface count rate less than that obtained in the first adsorption process. Subsequent removal of the gas following the second admission of [^{35}S]– sulphur labelled sulphur tetrafluoride resulted in a surface count rate similar to that obtained from the first desorption. This procedure was repeated three times using diferent samples of mercury(II) fluoride activated by hexafluoroacetone; a typical example of the behaviour of the [^{35}S]– sulphur surface count rate versus time during the

adsorption/desorption cycle is illustrated in figure 4.11.

A series of experiments using different initial pressures of [^{35}S]- sulphur labelled sulphur tetrafluoride in the range 10-250 Torr was carried out to determine the surface count rate and uptake of [^{35}S]- sulphur labelled sulphur tetrafluoride by the solid versus initial pressure of gas. In each experiment a fresh sample of hexafluoroacetone activated mercury(II) fluoride (1.5 g, 6.3 mmol) was used. The uptake of [^{35}S]- sulphur labelled sulphur tetrafluoride by the solid was calculated from the overall drop in the gas count rate before and after reaction. The variation of the surface count rate versus initial pressure is presented in figure 4.12 and the variation of [^{35}S]- sulphur labelled sulphur tetrafluoride uptake versus initial pressure is presented in figure 4.13 which showed that the amount of surface coverage was independent of the initial pressure at all pressures greater than 30 Torr.

After each reaction, the solid was evacuated for 1 h at room temperature and the permanently retained solid count rate was determined. The results obtained of the reaction between [^{35}S]- sulphur labelled sulphur tetrafluoride and mercury(II) fluoride activated by hexafluoroacetone are summarised in table 4.7. The overall uptake of [^{35}S]- sulphur labelled sulphur tetrafluoride by mercury(II) fluoride activated by hexafluoroacetone was considerably smaller at a given initial pressure than that of [^{36}Cl]- chlorine labelled chlorine monofluoride.

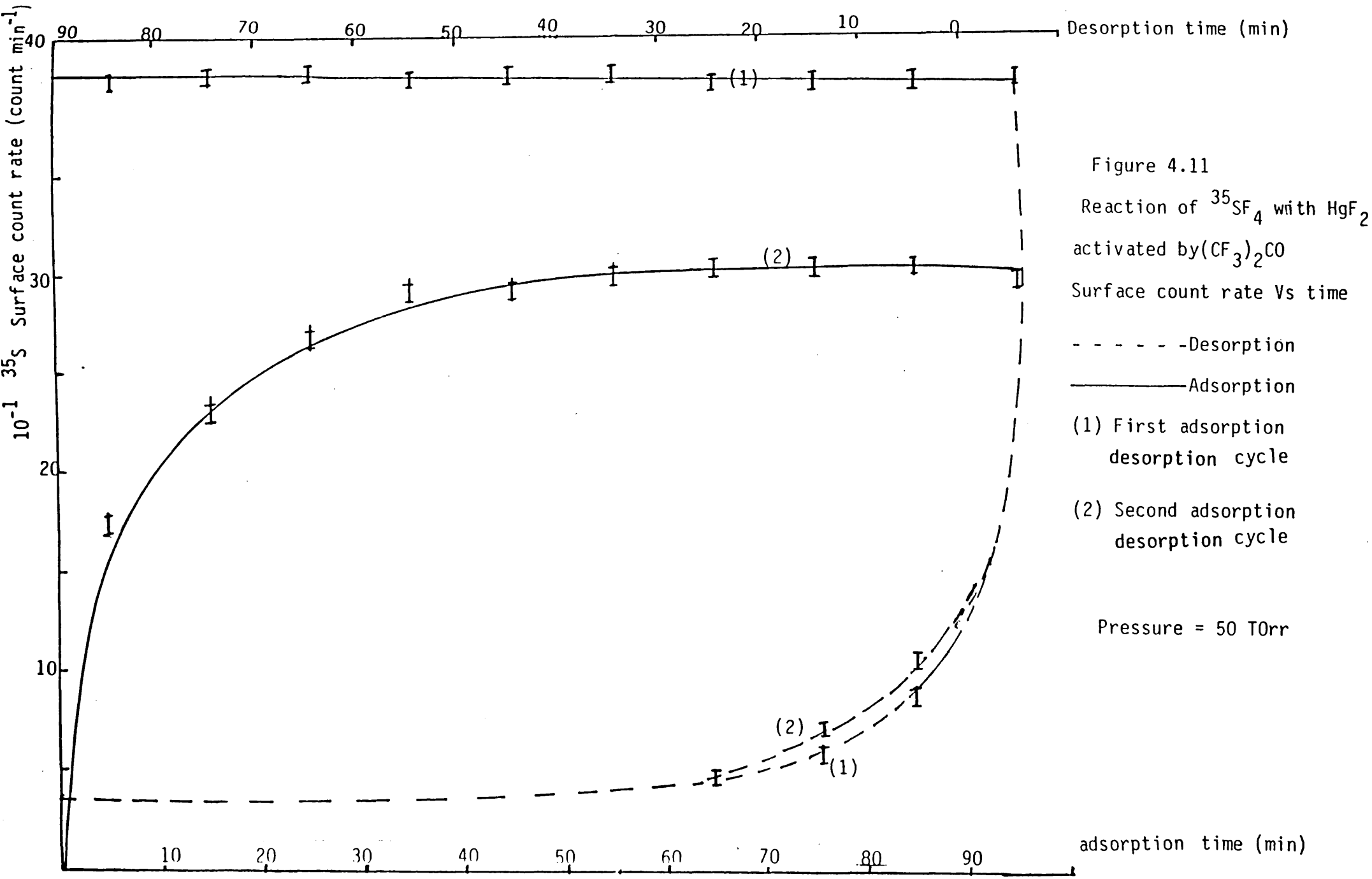


Figure 4.11

Reaction of $^{35}SF_4$ with HgF_2 activated by $(CF_3)_2CO$

Surface count rate Vs time

- - - - - -Desorption

————Adsorption

(1) First adsorption desorption cycle

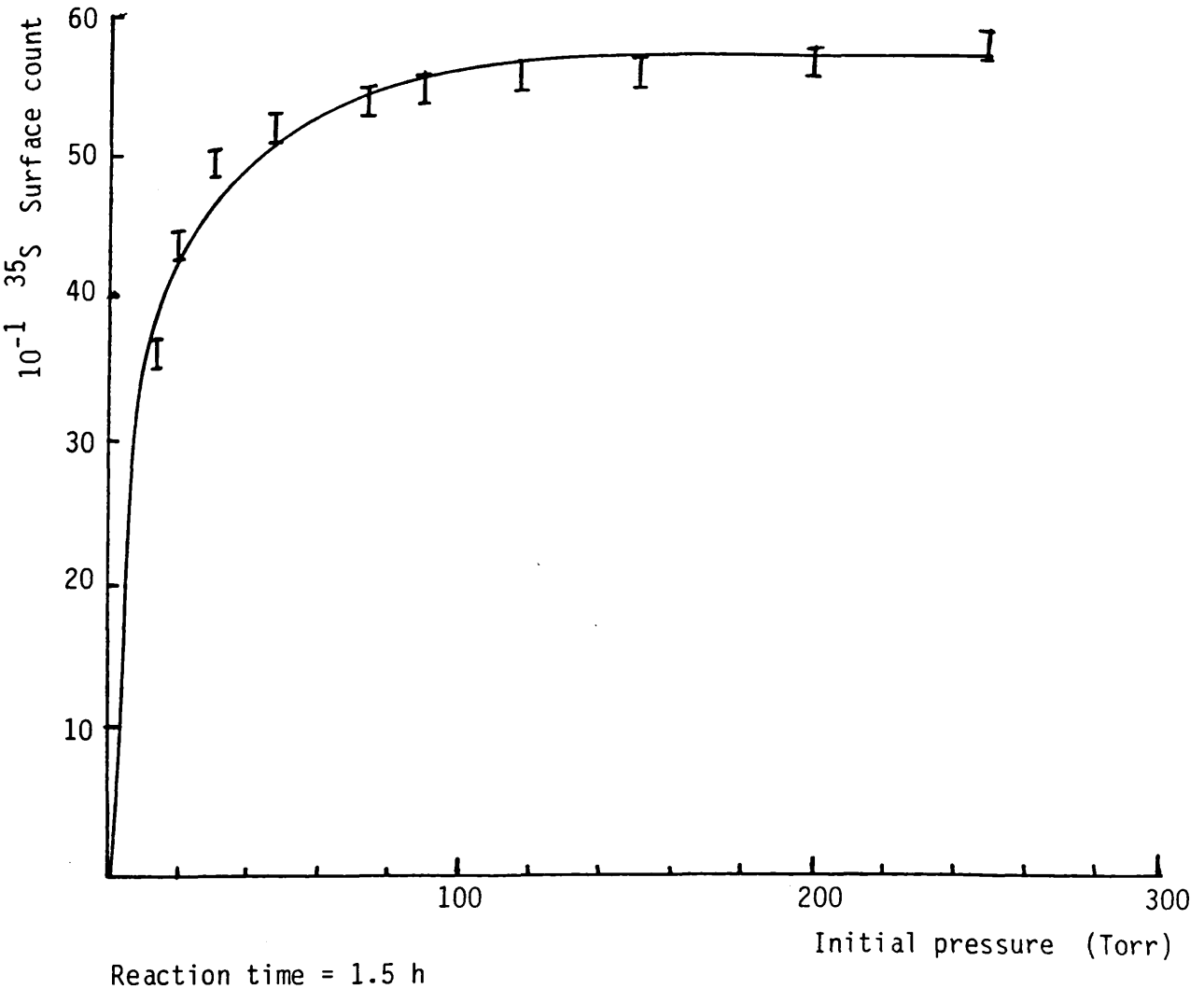
(2) Second adsorption desorption cycle

Pressure = 50 TOrr

Figure 4.12

Reaction of $^{35}SF_4$ with HgF_2 activated by$(CF_3)_2CO$

Variation of surface count rate Vs initial pressure of gas



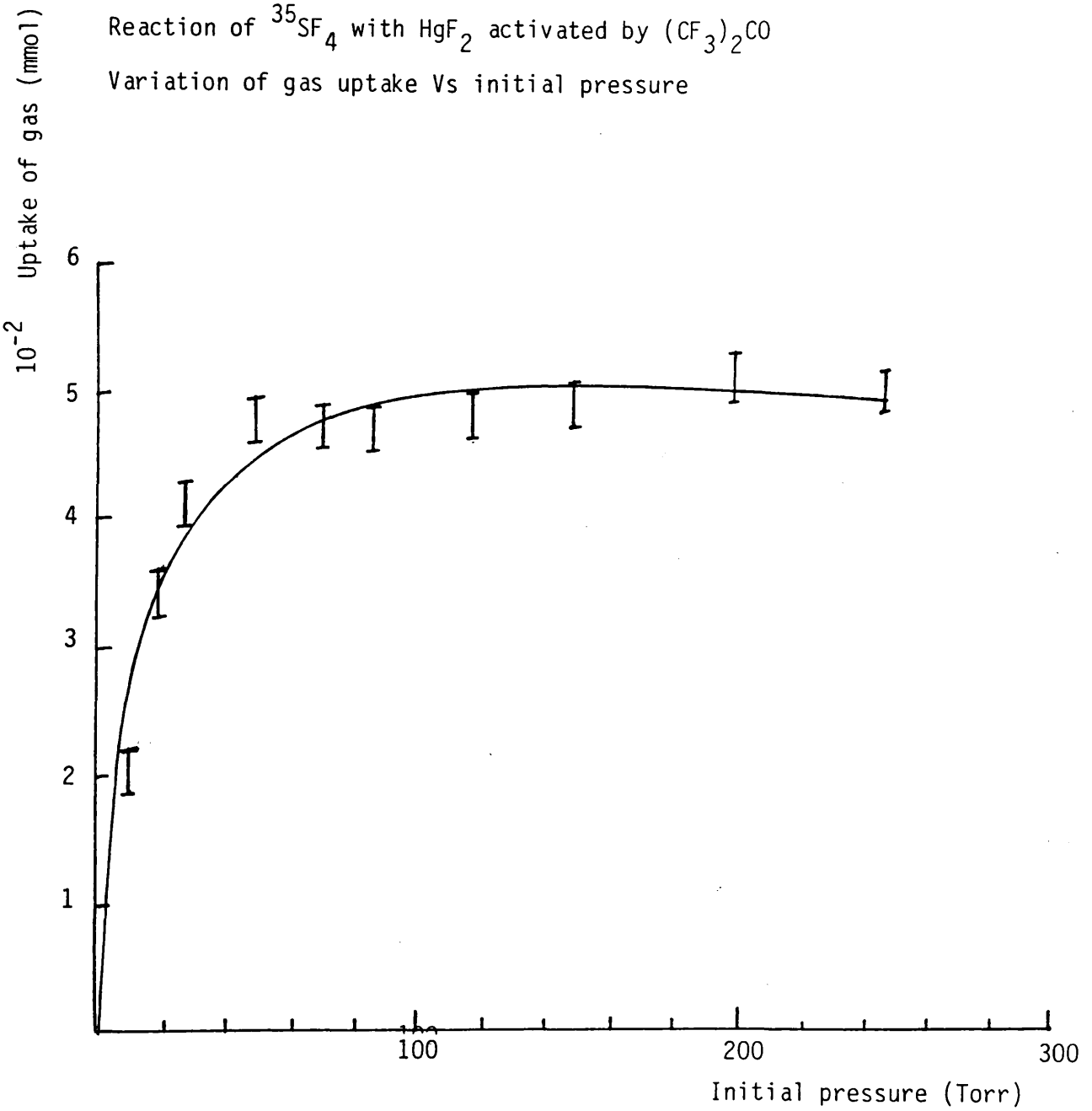
Reaction time = 1.5 h

Sample weight = 1.5 g

Figure 4.13

Reaction of $^{35}SF_4$ with HgF_2 activated by $(CF_3)_2CO$

Variation of gas uptake Vs initial pressure



Reaction time = 1.5 h

Sample weight = 1.5 g

Table 4.7

Summary of results of reaction of $[^{35}S]$-SF_4 with HgF_2 activated by $(CF_3)_2CO$

Inital pressure Torr	Total uptake of gas mmol	Surfacecount rate count min^{-1}
10 ± 0.5	0.021 ± 0.001	369 ± 16
20 ± 0.5	0.032 ± 0.001	467 ± 17
30 ± 0.5	0.039 ± 0.001	498 ± 17
50 ± 0.5	0.046 ± 0.002	524 ± 17
70 ± 0.5	0.045 ± 0.002	532 ± 17
90 ± 0.5	0.044 ± 0.002	546 ± 17
120 ± 0.5	0.047 ± 0.002	551 ± 17
150 ± 0.5	0.048 ± 0.002	542 ± 17
200 ± 0.5	0.051 ± 0.002	537 ± 17
250 ± 0.5	0.047 ± 0.002	553 ± 17

Sample weight = 1.5 g

Reaction time = 1.5 h

4.4 Reaction of Sulphur Chloride Pentafluoride with Mercury(II) Fluoride

The reaction between sulphur chloride pentafluoride and mercury(II) fluoride was studied using [^{35}S]- sulphur labelled sulphur chloride pentafluoride and [^{36}Cl]- chlorine labelled sulphur chloride pentafluoride.

The uptake of the gas by mercury(II) fluoride activated by hexafluoroacetone, as measured from the decrease in the gas phase count rate, was very small and not reliable. A very small surface count rate was obtained after allowing the [^{35}S]- sulphur labelled sulphur chloride pentafluoride or [^{36}Cl]- chlorine labelled sulphur chloride pentafluoride to react at room temperature with mercury(II) fluoride (1.5 g, 6.3 mmol) for 2 h. However, in each case the count rate decreased to background level on evacuation at room temperature.

4.5 Discussion

Chlorine monofluoride reacts at room temperature with mercury(II) fluoride both activated by hexafluoroacetone and pretreated with sulphur tetrafluoride. The overall uptake of chlorine monofluoride by hexafluoroacetone activated mercury(II) fluoride is much higher than that obtained with mercury(II) fluoride pretreated with sulphur tetrafluoride. The ratio of the uptake was 15:1 which is consistent with the ratio of the B.E.T areas of the solids described in chapter 3. Radiotracer experiments using [^{36}Cl]- chlorine labelled chlorine monofluoride showed that the

uptake of chlorine monofluoride by mercury(II) fluoride is reversible to some extent at room temperature. The count rate of the surface decreases very slowly on evacuation at room temperature, figure 4.4. After evacuation of the solid overnight, 45% of the activity is removed, and 55% of the [^{36}Cl]- chlorine surface activity is due to permanantly adsorbed species.

Lewis acid behaviour of chlorine monofluoride towards some Lewis base alkali metal fluorides as well as non metal fluorides, has been reported in the literature[38,39]. Alkali metal difluorochlorates(I), $M^+ ClF_2^-$ are well known, and evidence for the formation of the $Cs^+ ClF_2^-$ ion pair has been reported from infrared and Raman spectroscopic studies of the reaction between caesium fluoride and chlorine monofluoride in an argon matrix at 15 K[105]. Christe and coworkers reported that the difluorochlorates(I) have good thermal stability[38]. The stability order follows the sequence $CsClF_2 > RbClF_2 > KClF_2$. The decomposition of these difluorochlorates(I) occurs exothermically at 262, 248 and 237 °C respectively. The decrease in cation size and the increase in polarising power from Cs^+ to K^+ probably accounts for this order of stability[38].

Studies carried out in this department involving [^{36}Cl]- chlorine labelled chlorine monofluoride indicated that the uptake of chlorine monofluoride by caesium fluoride is irreversible at room temperature[72]. It would seem therefore that chlorine monofluoride acts in a similar manner with mercury(II) fluoride forming the difluorochlorates of mercury, the formation of which is responsible for the count rate observed on the surface of the solid. The difluorochlorates of mercury apparently have not

been reported in the literature.

Unlike caesium fluoride, a considerable amount of the adsorbed species is removed by evacuation of the solid at room temperature. Since the desorption process is very slow and only 45% of the activity is removed by evacuation overnight, it is not likely that the species removed is simply weakly adsorbed chlorine monofluoride. The decrease in the surface count rate might be better explained by the slow decomposition of the difluorochlorates salt formed. The surface count rate remaining after evacuation overnight is due to permanantly retained species, that is species stable at room temperature are also involved. Therefore it is possible that ClF_2^- is present in two different lattice types $HgF(ClF_2)$ and $Hg(ClF_2)_2$. One is stable at room temperature and the other is relatively unstable.

The instability observed for the difluorochlorates of mercury is in agreement with the effect of the cation size found with the alkali metal fluorides, in which the more stable salt of metal difluorochlorate is found with the largest cation, the less stable salts are those with a small cation size. The cation size of Hg^{++} (1.10 Å)[52] is much less than that of Cs^+ in the fluoride. The 2+ charge of the mercury cation and its small size greatly enhance the polarizing power of Hg^{++} which may account for the instability of the difluorochlorates(II) of mercury. Therefore, it seems resonable that the difluorochlorates of mercury would be less stable than that of caesium.

The admission of sulphur tetrafluoride to mercury(II) fluoride, pretreated with $[^{36}Cl]$-chlorine labelled chlorine monofluoride and

subsequently evacuated overnight, does not alter the surface count rate. The significant amount of [^{36}Cl]- chlorine labelled chlorine monofluoride that is retained is not displaced by sulphur tetrafluoride and sulphur tetrafluoride does not react with $Hg(ClF_2)_2$.

The reaction of [^{35}S]- sulphur labelled sulphur tetrafluoride with activated mercury(II) fluoride results in an uptake considerably less than the uptake obtained with chlorine monofluoride. Moreover, the uptake of sulphur tetrafluoride by mercury(II) fluoride is reversible at room temperature and most of the count rate of the surface is removed by evacuation at room temperature. The desorption process is very rapid in comparison with the desorption of chlorine monofluoride. This indicates that the species removed was weakly bound sulphur tetrafluoride. The count rate remaining on the solid surface after evacuation is due to the strongly bonded species that is permanantly adsorbed. The two possible structures of weakly bonded sulphur tetrafluoride, as derived from the structure of pentafluorosulphate, are shown in figure 4.14 and 4.15. The pentafluorosulphate anion has been characterised as having C_{4v} symmetry[29]. The more likely structure of the weakly bonded species is that shown in figure 4.14.

Most of the adsorbed [^{35}S]- sulphur labelled sulphur tetrafluoride is removed readily at room temperature. This sulphur tetrafluoride should not behave as a catalyst poison.

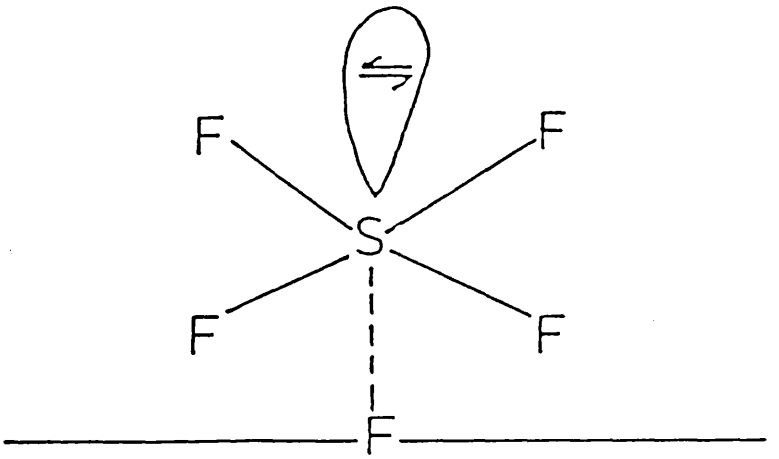
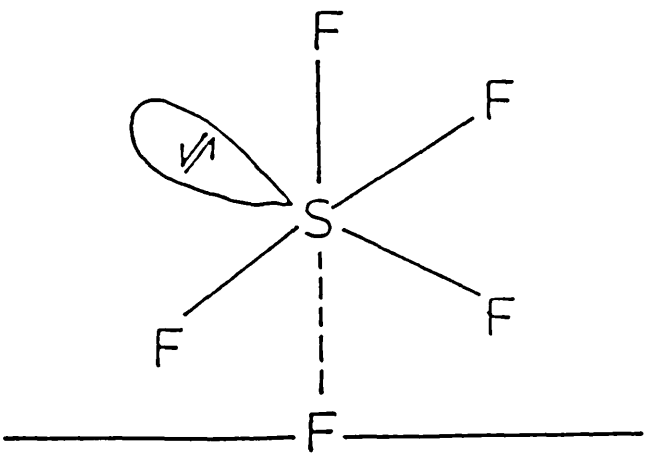


Figure 4.14

Possible structure of adsorbed SF_4

Figure 4.15

Possible structure of adsorbed SF_4



CHAPTER FIVE

CHAPTER FIVE

The Chlorofluorination of Sulphur Tetrafluoride

Introduction

Ionic metal fluorides participate in addition or oxidative addition reactions involving organic and inorganic fluorine compounds. For example, caesium fluoride catalyses the chlorofluorination of sulphur tetrafluoride by chlorine monofluoride[70]. The exchange ability of [^{18}F]- fluorine labelled sulphur tetrafluoride with mono and difluorides including mercury(II) fluoride was reported in previous work[103]. The existence of a correlation between the ^{18}F exchange ability and the catalytic activity for the chlorofluorination of sulphur tetrafluoride was also reported[104]. However, the correlation is not general for fluoride of other groups, these appears to be no correlation between, the exchange ability and any single cation property or the structural type[103].

In order to examine the catalytic activity of mercury(II) fluoride, the reaction between sulphur tetrafluoride and chlorine monofluoride in the presence of mercury (II) fluoride has been studied using [^{35}S]- sulphur labelled sulphur tetrafluoride, [^{36}Cl]- chlorine labelled chlorine monofluoride and by a conventional manometric method.

5.1 Experimental

All operations in which the radiochemically labelled species sulphur tetrafluoride and chlorine monofluoride were involved were carried out in the Pyrex vacuum system described in section 2.1.1 a. Reactions involving non-radioactive material were carried out in the Monel metal line, (passivated with chlorine trifluoride before use), described in section 2.1.1 b. Sulphur chloride pentafluoride was separated by low temperature trap to trap distillation as described in section 2.2.8 and identified by its infrared spectrum. Mercury(II) fluoride was added to the reaction vessel in the same way as described in section 4.1. [^{36}Cl]-Chlorine labelled chlorine monofluoride and [^{35}S]-sulphur labelled sulphur tetrafluoride were mixed in an appropriate ratio in a Monel metal pressure vessel before admission to the reaction vessel. When non-radioactive gases were used, mercury(II) fluoride was placed in the inert atmosphere box in a Monel metal pressure vessel. The vessel was then transferred to the Monel metal line and subsequently evacuated. An approprate reaction mixture containing chlorine monofluoride and sulphur tetrafluoride was condensed onto mercury(II) fluoride at low temperature and the mixture was then allowed to warm to room temperature.

5.2 Reaction of Chlorine Monofluoride with Sulphur Tetrafluoride over Mercury(II) Fluoride

5.2.1 Reaction of Chlorine Monofluoride with Sulphur Tetrafluoride over Untreated Mercury(II) Fluoride

A mixture of sulphur tetrafluoride (4.0 mmol) and chlorine monofluoride (4.0 mmol) was admitted to a sample of mercury(II) fluoride (2.0 g, 8.4 mmol). After allowing the mixture to react at room temperature for 2 h, the volatile material was removed and separated into the individual components. The infrared spectrum of the gas separated from chlorine monofluoride showed no evidence for the presence of sulphur chloride pentafluoride and bands attributed to thionyl fluoride and silicon tetrafluoride were present. The attempted reaction of sulphur tetrafluoride with chlorine monofluoride over untreated mercury(II) fluoride was attempted several times. In each case, a fresh sample of mercury(II) fluoride was used and no sulphur chloride pentafluoride was obtained. This was probably due to the hydrolysis of the reactants by water present on the surface of mercury(II) fluoride.

5.2.2 Reaction of Sulphur Tetrafluoride with Chlorine Monofluoride over Mercury(II) Fluoride Activated by Hexafluoroacetone

The admission of a mixture of sulphur tetrafluoride (4.0 mmol) and chlorine monofluoride (4.0 mmol) to a sample of mercury(II) fluoride (2.0 g, 8.4 mmol) activated by hexafluoroacetone at room temperature, led to different results from those obtained in the above reaction. Sulphur chloride pentafluoride was obtained in the presence of mercury(II) fluoride activated by hexafluoroacetone. Sulphur tetrafluoride and chlorine monofluoride were

added to mercury(II) fluoride activated by hexafluoroacetone and allowed to react at room temperature for 1 h. After this time of reaction the volatile material was removed and sulphur chloride pentafluoride was separated from unreacted chlorine monofluoride and sulphur tetrafluoride. The yield of sulphur chloride pentafluoride as determined from pressure measurements was ca 75 % after 1 h of reaction. The admission of a further sample of the mixture (1:1 mole ratio) to the same sample of mercury(II) fluoride under the same conditions yielded to the same results. Several reactions using a 1:1 mole ratio of sulphur tetrafluoride and chlorine monofluoride were carried out using the same sample of catalyst. No effect on the yield was observed, that is the yield remained constant. The results obtained using different initial pressures are listed in table 5.1.

The reaction of the mixture of sulphur tetrafluoride and chlorine monofluoride was studied using different mole ratios. In each experiment, a fresh sample of mercury(II) fluoride, activated by hexafluoroacetone, was used and the appropriate mixture was obtained by keeping one of the reactants constant and varying the other. The results of the experiments in which sulphur tetrafluoride was kept constant at 3.5 mmol and chlorine monofluoride was varied from 0.5 to 3.5 mmol are summarised in table 5.2 and are shown schematically in figure 5.1. The yield of sulphur chloride pentafluoride was affected by the mole ratio used. A maximum yield from the reaction between sulphur tetrafluoride and chlorine monofluoride in the presence of mercury(II) fluoride activated by hexafluoroacetone was obtained at a 1:1 mole ratio with a minimum retention of gas. A remarkable increase of the fraction of gas retained was obtained when the quantity of chlorine monofluoride in the mixture was

Table 5.1

The yield of SF_5Cl utilising HgF_2 activated by $(CF_3)_2CO$

Run	Batch	Sample	Gas admitted equimolar ClF + SF_4 mmol	yield %
1	1	1	8.0	75
2	1	1	8.0	74
3	1	1	8.0	75
4	2	1	8.0	77
5	2	1	6.0	76
6	2	2	6.0	77
7	3	1	8.0	75
8	3	2	6.0	76
9	3	3	6.0	74

Sample weight = 2.0 g

Reaction time = 1 h

Batch numbers correspond to three pretreatments

Table 5.2

Reaction of ClF with SF_4 over HgF_2 activated by $(CF_3)_2CO$

The competition reaction results

ClF = 0.5——3.5 mmol

SF_4 = 3.5 mmol

ClF admitted	Gas retained ClF + SF_4	SF_5Cl	Gas recovered ClF + SF_4
mmol	mmol	mmol	mmol
0.5	0.61	0.09	3.21
1.0	0.60	0.24	3.42
1.5	0.53	0.45	3.57
2.0	0.47	0.76	3.51
2.5	0.37	1.15	3.33
3.0	0.22	1.65	2.98
3.5	0.00	2.66	1.68

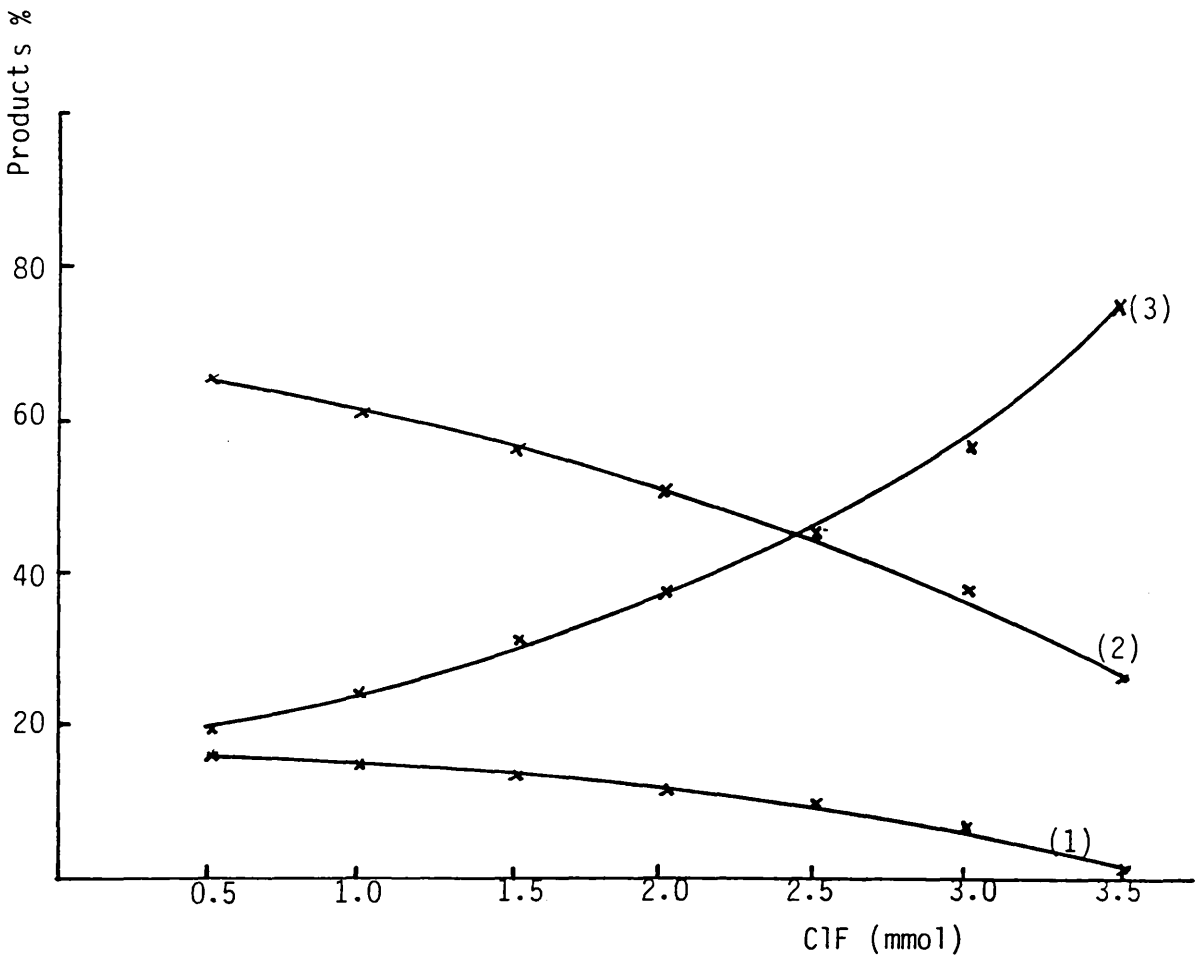
Sample weight = 2.0 g

Figure 5.1

Change in % composition for SF_4 + ClF ⟶ SF_5Cl

over HgF_2 activated by $(CF_3)_2CO$

$SF_{4=}$ = 3.5 mmol



(1) ClF + SF_4 retained

(2) ClF + SF_4 gas

(3) SF_5Cl gas

greater than the quantity of sulphur tetrafluoride. However, the fraction of gas, sulphur tetrafluoride and chlorine monofluorde, retained at low mole ratio that is with chlorine monofluoride equal to 0.5 mole was relatively small.

The effect on the yield of sulphur chloride pentafluoride and the fraction of sulphur tetrafluoride plus chlorine monofluride retained by mercury(II) fluoride, was also tested by keeping the quantity of chlorine monofluoride constant at 0.5 mmol and varying the quantity of sulphur tetrafluoride from 0.5 to 3.5 mmol. The fraction of chlorine monofluoride and sulphur tetrafluoride retained by the solid decreased as the quantity of sulphur tetrafluoride in the mixture incresed. The results obtained when sulphur tetrafluoride was varied from 0.5 to 3.5 mmol while chlorine monofluoride kept constant are summarised in table 5.3 and shown in figure 5.2.

The nature of the chlorofluorination of sulphur tetrafluoride, catalysed by mercury(II) fluoride, activated by hexafluoroacetone, was examined using the radiotracer method. The uses of ^{35}S or ^{36}Cl were explored in the reaction using mixtures containing $[\,^{35}S\,]$– sulphur labelled sulphur tetrafluoride or $[\,^{36}Cl\,]$– chlorine labelled chlorine monofluoride. A mixture, 1:1 ratio, of $[\,^{36}Cl\,]$– chlorine labelled chlorine monofluoride and sulphur tetrafluoride was admitted to a sample of mercury(II) fluoride (1.5 g, 6.3 mmol) activated by hexafluoroacetone. The $[\,^{36}Cl\,]$– chlorine surface count rate was followed with time and is presented in figure 5.3. This shows that a large $[\,^{36}Cl\,]$– chlorine surface count rate was recorded at the first reading followed thereafter by a very rapid decrease. A constant value was

Table 5.3

Reaction of ClF with SF_4 over HgF_2 activated by $(CF_3)_2CO$

The competition reaction results

ClF = 3.5 mmol

SF_4 = 0.5——3.5 mmol

SF_4 admitted mmol	Gas retained mmol	SF_5Cl mmol	Gas recovered mmol
0.5	0.81	0.12	3.06
1.0	0.84	0.26	3.46
1.5	0.77	0.43	3.79
2.0	0.67	0.70	4.13
2.5	0.54	1.02	4.44
3.0	0.38	1.71	4.42
3.5	0.00	2.69	2.10

sample weight = 2.0 g

Figure 5.2

Change in % composition for SF_4 + ClF ⟶ SF_5Cl over HgF_2 activated by $(CF_3)_2CO$

ClF = 3.5 mmol

(1) ClF + SF_4 retained
(2) ClF + SF_4 gas
(3) SF_5Cl gas

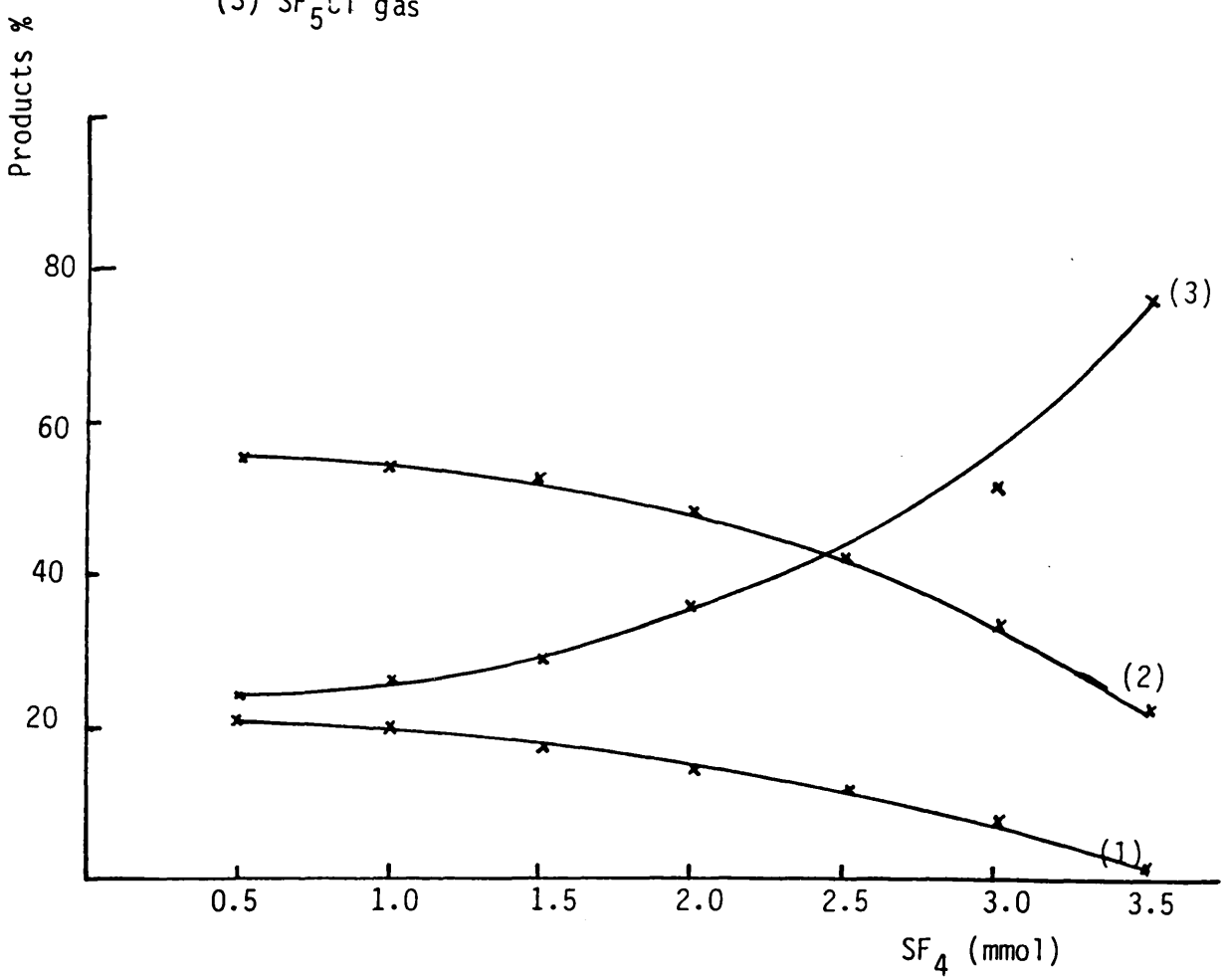
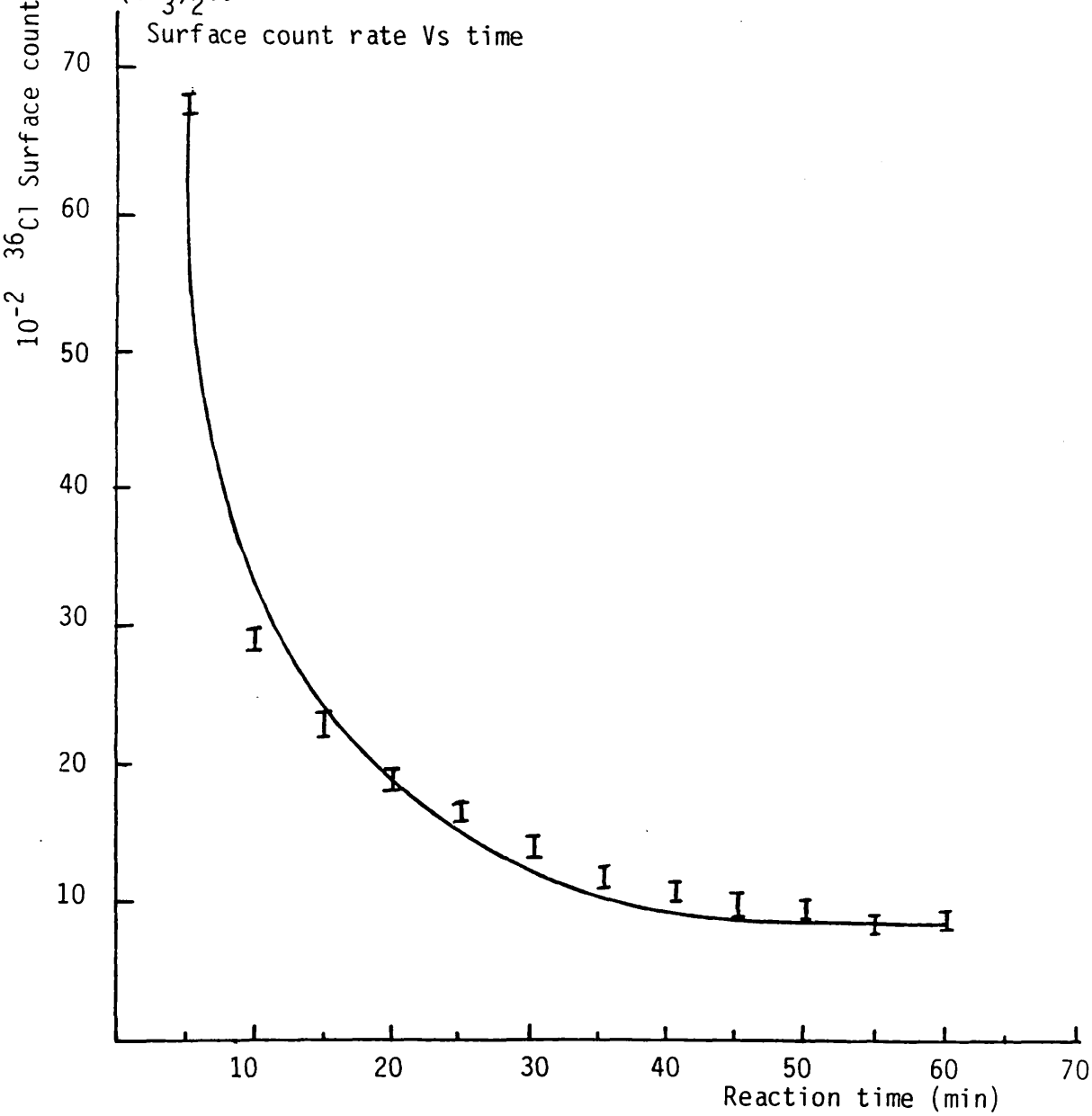


Figure 5.3

Reaction of $^{36}ClF + SF_4$, 1:1 mole ratio over HgF_2 activated by $(CF_3)_2CO$



Pressure = 400 Torr

observed after ca. 40 minutes. Evacuation of the system after the reaction resulted in the surface count rate being almost equivalent to the background count rate of the Geiger Müller counter. Further admission of a mixture of 1:1 mole ratio to the same sample of mercury(II) fluoride under the same conditions gave results similar to those described above. The removal of the gas phase resulted in the $[\,^{36}Cl\,]$- chlorine surface count rate falling to the background count rate.

The decrease in $[\,^{36}Cl\,]$- chlorine surface count rate in the above reaction was tested for first and second order kinetic behaviour, taking the initial reading of the $[\,^{36}Cl\,]$- chlorine surface count rate as $t = 0$, table 5.4. The analysis showed that the chlorofluorination of sulphur tetrafluoride by chlorine monofluoride did not occur according to a first order reaction. However, a plot of the second order relationship was constructed and the graph obtained, which is presented in figure 5.4, was linear. Therefore the chlorofluorination of sulphur tetrafluoride by chlorine monofluoride follows a second order reaction under the conditions used.

A similar procedure was used with $[\,^{35}S\,]$- sulphur labelled sulphur tetrafluoride as the labelled gas. The admission of a 1:1 mole ratio mixture of chlorine monofluoride and $[\,^{35}S\,]$- sulphur labelled sulphur tetrafluoride to a sample of mercury(II) fluoride, activated by hexafluoroacetone, exhibited the same characteristics as those described for the mixture of a 1:1 mole ratio of $[\,^{36}Cl\,]$- chlorine labelled chlorine monofluoride and sulphur tetrafluoride. The highest $[\,^{35}S\,]$- sulphur surface count rate was recorded at the first reading after admission of the mixture to mercury(II) fluoride, followed therafter by a rapid decrease during the first 30 minutes,

Table 5.4

Summary of the results of the reaction of [^{36}Cl]-ClF and SF_4 over HgF_2 activated by $(CF_3)_2CO$

Time min	Surface count rate count min^{-1}	$(CR_0 - CR)/CR_0.CR \times 10^5$
05	6834 ± 63	0.00
10	2984 ± 59	18.87
15	2321 ± 57	28.45
20	1937 ± 57	36.99
25	1634 ± 56	46.56
30	1416 ± 56	55.98
35	1251 ± 52	65.30
40	1116 ± 50	74.97
45	1061 ± 49	79.61
50	915 ± 49	94.65
55	842 ± 49	104.13
60	784 ± 49	112.91

CR_0 = 6834

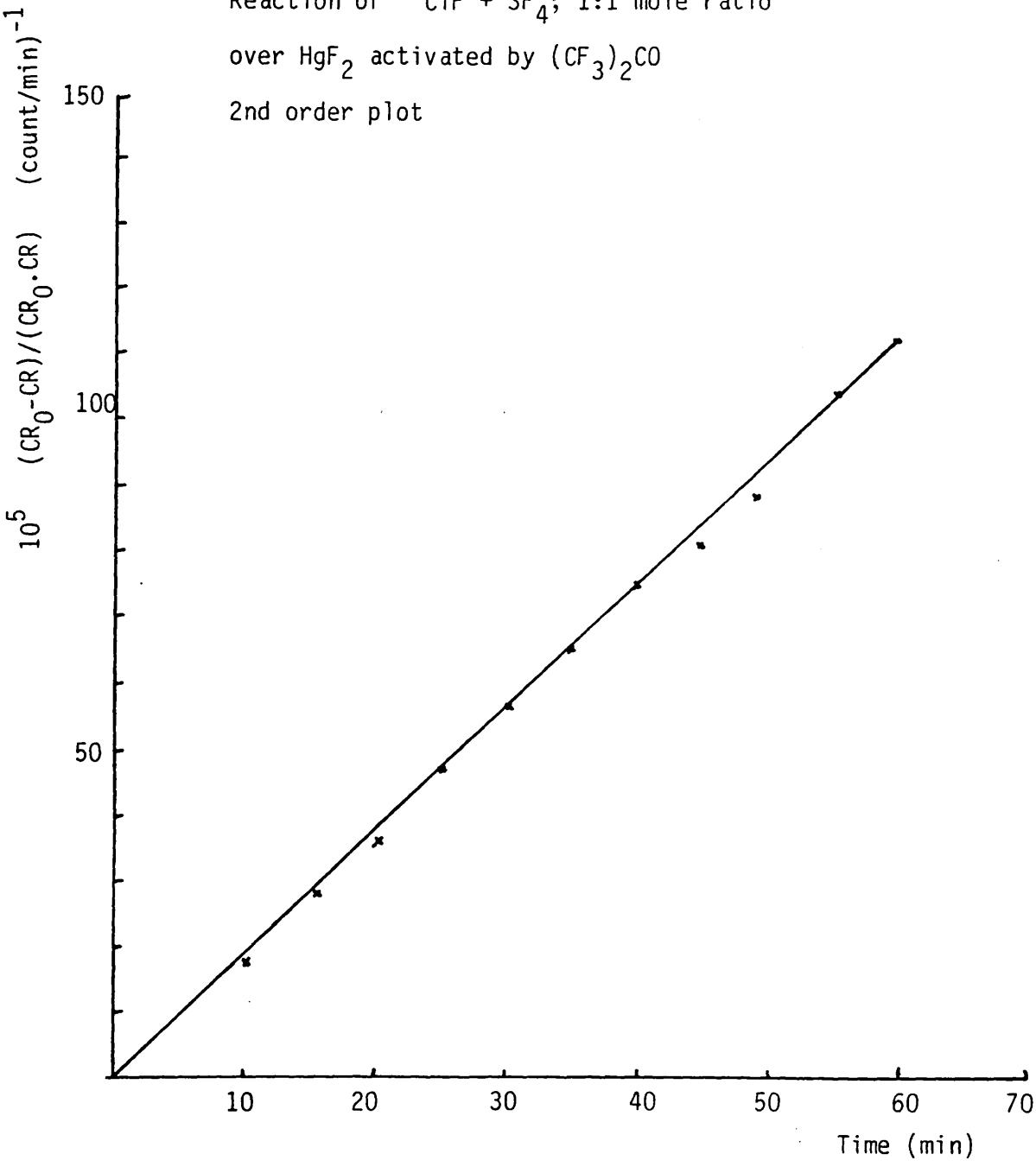
CR_0 = Initial reading of the surface count rate

CR = Surface count rate at time = t

Figure 5.4

Reaction of $^{36}ClF + SF_4$; 1:1 mole ratio over HgF_2 activated by $(CF_3)_2CO$

2nd order plot



then it remained almost constant. The [^{35}S]- sulphur surface count rates at different times are listed in table 5.5 and are shown in figure 5.5.Evacuation of the solid at room temperature led to a drop in the surface count rate equal to the background count rate of the Geiger Müller counter, that is the activity of the solid was completely removed. Admission of a further sample of the mixture of 1:1 mole ratio to the same sample of mercury(II) fluoride followed the same pattern as in the first reaction. The decrease in [^{35}S]- sulphur surface count rate during the reaction of the mixture of 1:1 mole ratio of [^{35}S]- sulphur labelled sulphur tetrafluoride was tested for its kinetic behaviour, table 5.5. The plots of the second order relationship, $(CR_0 - CR)/(CR_0.CR)$ versus time, constructed were straight lines, where CR_0 is the initial reading of the surface count rate and CR is the surface count rate at time equal t. A typical example of this plot is shown in figure 5.6. This indicated that the chlorofluorination of sulphur tetrafluoride by chlorine monofluoride follows a second order reaction which confirmed the results obtained from the mixture of 1:1 mole ratio of [^{36}Cl]- chlorine labelled chlorine monofluoride and sulphur tetrafluoride.

5.2.3 Reaction of Chlorine Monofluoride with Mercury(II) Fluoride Activated with Hexafluoroacetone and Pretreated with [^{35}S]- Sulphur Labelled Sulphur Tetrafluoride.

Chlorine monofluoride (6.0 mmol) was admitted to a sample of activated mercury(II) fluoride (1.5 g, 6.3 mmol) previously reacted with [^{35}S]- sulphur labelled sulphur tetrafluoride. The chlorine monofluoride was allowed to react for 1.5 h at room temperature. When the volatile

Table 5.5

Summary of the results of the reaction of [^{35}S]-SF_4 with ClF, 1:1 mole ratio over HgF_2 activated by $(CF_3)_2CO$

Time min	Surface count rate count min^{-1}	$(CR_0 - CR)/CR_0.CR \times 10^4$
05	718 ± 43	0.00
10	451 ± 38	08.21
15	288 ± 37	20.74
20	242 ± 36	28.35
25	198 ± 33	36.42
30	173 ± 31	43.61
35	153 ± 29	51.02
40	145 ± 29	54.92
45	132 ± 28	61.37
50	120 ± 28	68.73
55	108 ± 28	78.43
60	105 ± 28	81.02

CR_0 = 718 count min^{-1}

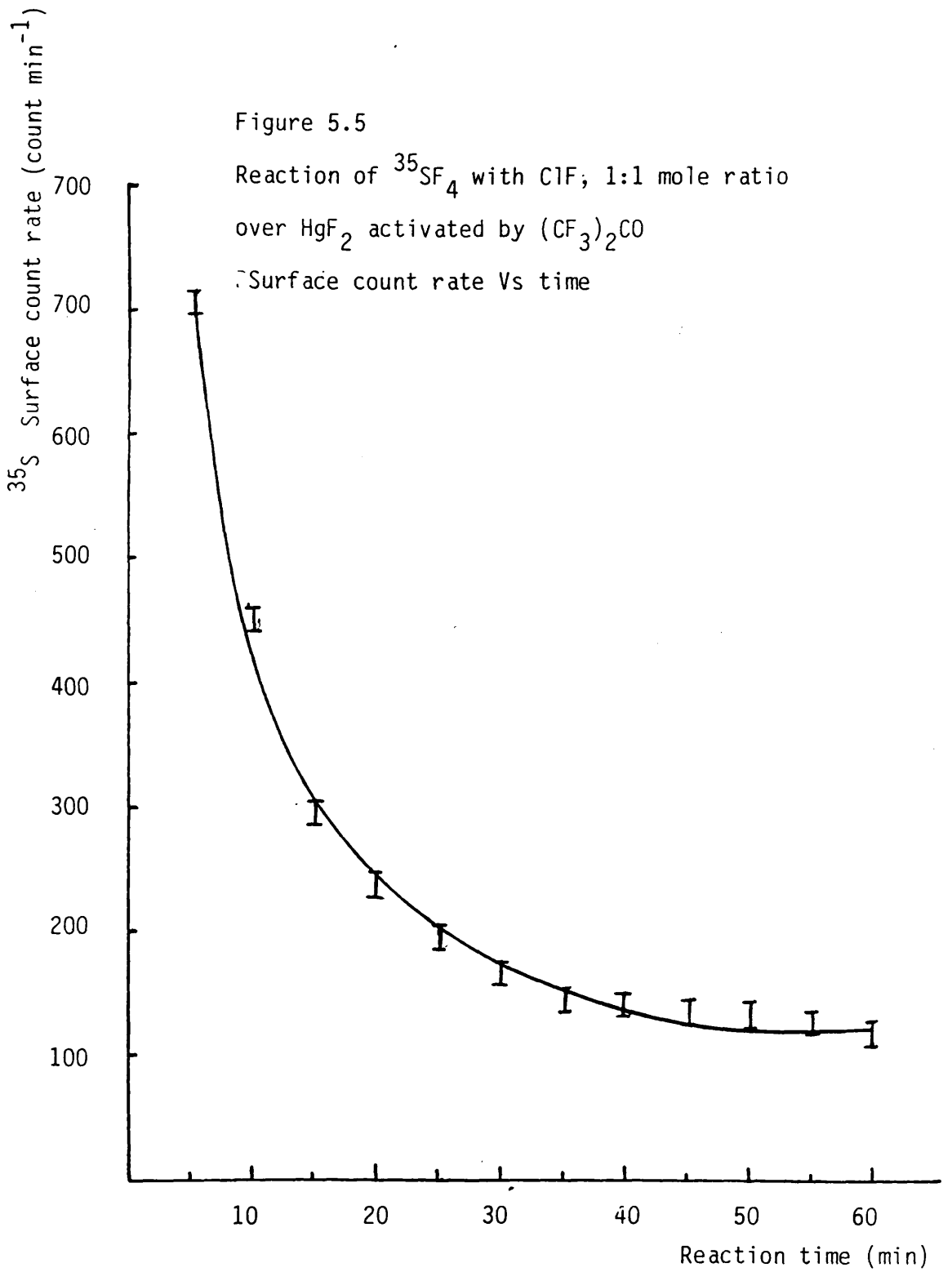
CR_0 = Initial reading of the surface count rate

CR = Surface count rate at time = t

Figure 5.5

Reaction of $^{35}SF_4$ with ClF; 1:1 mole ratio over HgF_2 activated by $(CF_3)_2CO$

Surface count rate Vs time

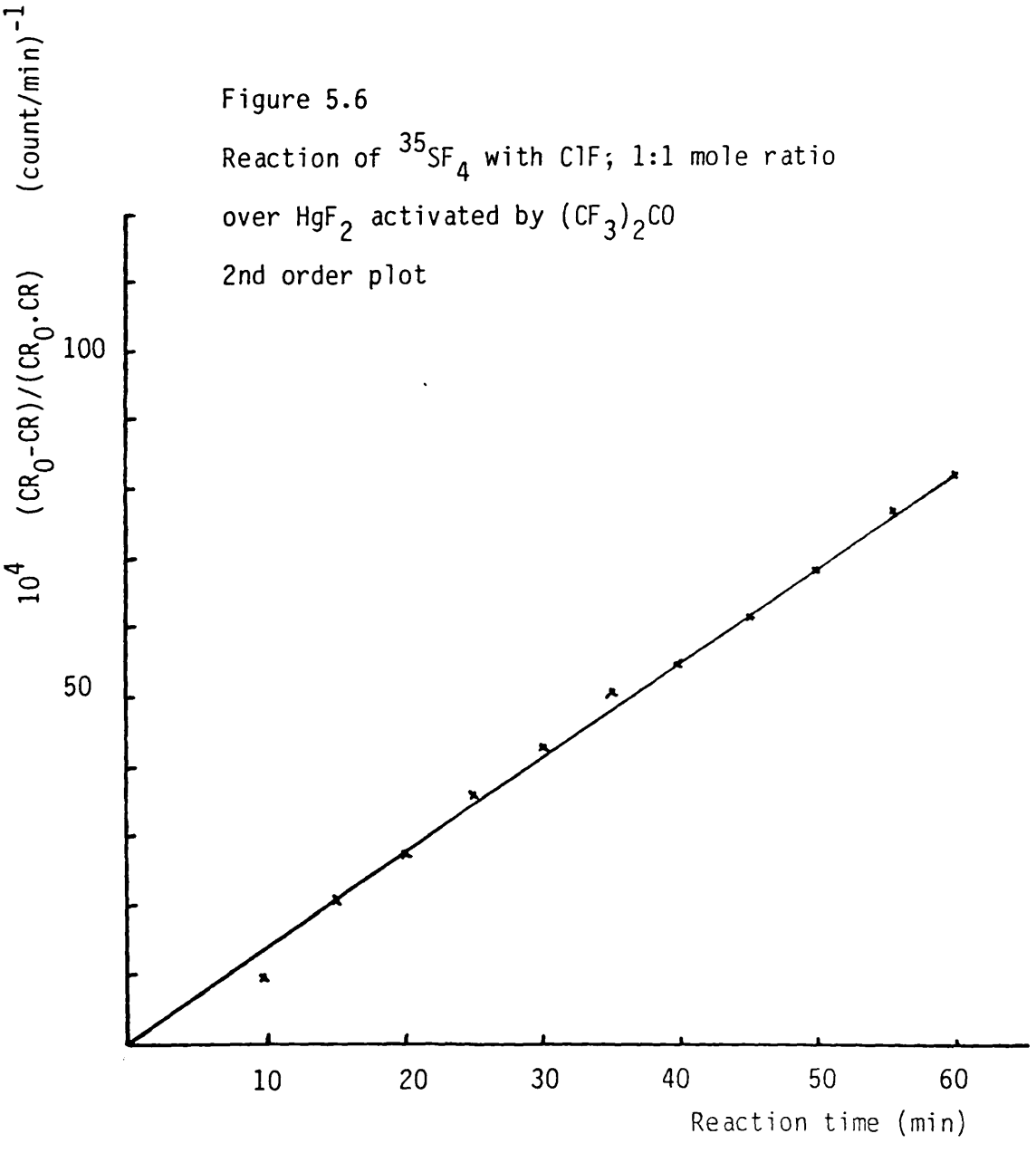


Pressure = 400 Torr

Figure 5.6

Reaction of $^{35}SF_4$ with ClF; 1:1 mole ratio over HgF_2 activated by $(CF_3)_2CO$

2nd order plot



material was removed, the surface count rate dropped to the background count rate. The [^{35}S]- sulphur activity of the solid remaining after treatment of mercury(II) fluoride with [^{35}S]- sulphur labelled sulphur tetrafluoride and subsequent evacuation was removed by admission of chlorine monofluoride. This experiment was repeated using non labelled gases where sulphur tetrafluoride (200 Torr, 8.0 mmol) was admitted to a sample of mercury(II) fluoride activated by hexafluoroacetone (2.0 g, 8.4 mmol) and allowed to react at room temperature for 2 h. Unreacted sulphur tetrafluoride was removed and subsequently chlorine monofluoride (200 Torr, 8.0 mmol) was admitted to the sample of mercury(II) fluoride pretreated with sulphur tetrafluoride. After allowing chlorine monofluoride to react at room temperature for 2 h, volatile products were removed and chlorine monofluoride was separated by low temperature fractional condensation. The infrared spectrum of the gas remaining after this separation showed the presence of sulphur chloride pentafluoride. Since the quantity of sulphur tetrafluoride retained by mercury(II) fluoride was very small, it was difficult to determine quantitatively the sulphur chloride pentafluoride recovered in this reaction.

5.2.4 Reaction of Chlorine Monofluoride with Sulphur Tetrafluoride Over Mercury(II) Fluoride Pretreated with Sulphur Tetrafluoride

Due to the hydrolysis expected of the reactants over untreated mercury(II) fluoride, the commercial mercury(II) fluoride used in this section was pretreated with sulphur tetrafluoride as described in section 3.2.1. A mixture of a 1:1 mole ratio of sulphur tetrafluoride (4.0 mmol)

and chlorine monofluoride (4.0 mmol) was condensed onto a sample of mercury(II) fluoride. The reactants were allowed to react at room temperature for 4 h. After separation of the unreacted material, the infrared spectrum of the gas trapped at −80°C showed the presence of sulphur chloride pentafluoride. The procedure was repeated several times and each time the yield of sulphur chloride pentafluoride was determined. Table 5.6 summarises the yield of sulphur chloride pentafluoride obtained using both a fresh sample of the catalyst and a sample which had been previously used. The data obtained showed that the yield of sulphur chloride pentafluoride was not affected by the repeated addition of the mixture of 1:1 mole ratio. More importantly, the quantities of sulphur chloride pentafluoride obtained within the above reaction time were smaller than those obtained in the case of mercury (II) fluoride activated by hexafluoroacetone.

5.3 Discussion

The room temperature reaction between chlorine monofluoride and sulphur tetrafluoride in the presence of mercury(II) fluoride, pretreated with hexafluoroacetone or sulphur tetrafluoride, leads to the formation of sulphur chloride pentafluoride. However no sulphur chloride pentafluoride is obtained when this reaction is attempted over untreated mercury(II) fluoride. The lack of the formation of sulphur chloride pentafluoride is probably due to the hydrolysis of the reactants at the mercury(II) fluoride surface. Therfore one function of the pretreatment of mercury(II) fluoride is to produce anhydrous mercury(II) fluoride. The pretreatment process also affects the B.E.T area of the solid[92]. Thus sulphur chloride is obtained

Table 5.6

Reaction of ClF with SF_4 over HgF_2 pretreated with SF_4

The yield of SF_5Cl

Run	Batch	Sample	Gas admitted equimolar ClF + SF_4 mmol	SF_5Cl %
1	1	1	8.0	44
2	1	1	8.0	43
3	1	1	8.0	45
4	2	1	10.0	45
5	2	1	10.0	44
5	2	2	10.0	46
7	3	1	12.0	46
8	3	2	12.0	45
9	3	3	12.0	45

Sample weight = 2.0 g

Reaction time = 4 h

Batch numbers correspond to three pretreatments.

when the reaction is attempted over pretreated mercury(II) fluoride. The results presented in section 5.2.2 and section 5.2.4 show that the yield of sulphur chloride pentafluoride obtained in the case of mercury(II) fluoride pretreated with hexafluoroacetone is higher than that obtained using mercury(II) fluoride pretreated with sulphur tetrafluoride. This is probably due to the larger B.E.T area of mercury(II) fluoride activated by hexafluoroacetone which provides a greater number of contacts between the probe molecules, ClF and SF_4, and the active sites on the surface of mercury(II) fluoride. The yield of sulphur chloride pentafluoride obtained in 1 h with mercury(II) fluoride activated by hexafluoracetone is ca 75%. The yield obtained in 4 h with the pretreated sulphur tetrafluoride is ca 45%. However, the ratio of the B.E.T area is 15:1. This latter observation is in agreement with the work reported in the literature[72]. The reactivty of caesium fluoride is increased by its pretreatment with hexafluoroacetone and appears to enhance its abilty to react as Lewis base[72]. The pretreatment of caesium fluoride by hexafluoroacetone is the most effective way to increase its B.E.T area and enhance the catalytic activity for the chlorofluorination of sulphur tetrafluoride[92,72]

It appears from the results presented in table 5.4 and shown schematically in figure 5.3 that the chlorofluorination of sulphur chloride tetrafluoride over mercury(II) fluoride pretreated with hexafluoroacetone proceeds rapidly at room temperature. The results of the competitive reaction presented in table 5.2, 5.3 and shown in figure 5.1, 5.2 indicate that a high yield with no retention of gas is obtained for the mixture of 1:1 mole ratio. However at low concentration of sulphur tetrafluoride or chlorine monofluoride in the mixture, the retention of sulphur tetra fluoride and

chlorine monofluoride becomes significant. From the above results it can be suggested that the reaction involving adsorbed sulphur tetrafluoride, $HgF_2.SF_{4(ads)}$, and adsorbed chlorine monofluoride, $HgF_2.ClF_{(ads)}$, to form sulphur chloride pentafluoride is faster than the reaction of the adsorbed state of these molecules with fluoride ions to form strongly bonded species according to the following equations.

$$F^- .SF_{4(ads)} \longrightarrow SF_5^-(s)$$

$$F^- .ClF_{(ads)} \longrightarrow ClF_2^-(s)$$

CHAPTER SIX

CHAPTER SIX

DISCUSSION AND CONCLUSION

Sulphur chloride pentafluoride is successfully prepared at room temperature in the presence of caesium fluoride catalyst by the reaction of chlorine monofluoride with sulphur tetrafluoride[71]. The pretreatment given to the catalyst is found to be of great effect both on its B.E.T area and on the catalytic activty for the above reaction[72,92]. Similar behaviour has been found with mercury(II) fluoride. The pretreatment of mercury(II) fluoride with hexafluoroacetone as described in chapter 3 leads to a remarkable increase of its B.E.T area compared with the B.E.T area of mercury(II) fluoride pretreated with sulphur tetrafluoride. The formation of a porous structure as stated in chapter 3 and the dislocation of the crystal structure by the hexafluoroacetone molecule could account for this increase in the B.E.T area. Evidence from the infrared spectrum, discussed in chapter 3, indicates that there is a retention of hexafluoroacetone by mercury(II) fluoride, and the heptafluorisopropoxide salt is formed.

During the reaction of mercury(II) fluoride with hexafluoroacetone to form the heptafluoroisopropoxide anion, the crystal lattice must undergo some form of expansion to accomodate the large heptafluoroisoproxide anion. The isopropoxide is thermally unstable and no retention of hexafluoroacetone by mercury(II) fluoride is found after the thermal decomposition. A permanent alteration of the crystal structure as a result

of this process is unlikely. Unlike the situation for mercury(II) fluoride, retention of hexfluoroacetone to a small extent by caesium fluoride is observed after thermal decompsition of its adduct[94], but even in this case the disruption of the crystal structure by the presence of the heptafluoroisopropoxide anion, $(CF_3)_2FCO^-$, does not account for the overall increase of the B.E.T area[94]. Work carried out in this Department by K. Dixon and coworkers indicates that similar increase in the B.E.T area is obtained when caesium fluoride is pretreated whith carbonyl fluoride although the adduct formed is completely decomposed. The increase in the B.E.T area will provide a large contact between the solid that is the adsorbent and the reactive molecules, that is the adsorbate and therefore enhance the physical and chemical adsorption.

Consistent with the above hypothesis are the results obtained in chapter 4 from the study of adsorption of $[^{35}S]$- sulphur labelled sulphur tetrafluoride and $[^{36}Cl]$- chlorine labelled chlorine monofluoride. They indicate that very rapid and large uptakes of chlorine monofluoride and sulphur tetrafluoride are observed during the reaction of these molecules with mercury(II) fluoride pretreated with hexafluoroacetone. However, when mercury(II) fluoride pretreated with sulphur tetrafluoride is used, the uptakes of chlorine monofluoride and sulphur tetrafluoride are relatively slow and significantly less than those obtained with hexafluoroacetone pretreated mercury(II) fluoride. This is in a good agreement with the work reported by Kolta and coworkers, in which the pretreatments of caesium fluoride greatly enhance the uptake of chlorine monofluoride or sulphur tetrafluoride by the solid. Moreover the largest uptake is obtained with the largest B.E.T area of caesium fluoride[72].

The results presented in chapter 4 show that there is considerable retention of [^{36}Cl]- chlorine labelled chlorine monofluoride by mercury(II) fluoride surface, and that the retained species do not participate to any appreciable extent in the reaction with sulphur tetrafluoride to form sulphur chloride pentafluoride. This observation suggests that the weakly adsorbed chlorine monofluoride in the first step subsequently reacts with mercury(II) fluoride to form a chemical bond according to the following equations.

$$F^-_{(s)} + ClF_{(g)} \longrightarrow F^-.ClF_{(ads)} \qquad \text{Eq 5.1}$$

$$F^-.ClF_{(ads)} \longrightarrow ClF_2^-{}_{(s)} \qquad \text{Eq 5.2}$$

The behaviour of [^{35}S]- sulphur labelled sulphur tetrafluoride is similar to that of chlorine monofluoride, in that the uptake of sulphur tetrafluoride by mercury(II) fluoride is enhanced by the activation with hexafluoroacetone. However, the quantities involved with sulphur tetrafluoride are considerably less than those with chlorine monofluoride. The admission of chlorine monofluoride to mercury(II) fluoride pretreated with [^{35}S]- sulphur labelled sulphur tetrafluoride results in a total removal of the activity from the surface of the solid. The admission of chlorine monofluoride to sulphur tetrafluoride pretreated catalyst leads to the complete conversion of retained sulphur tetrafluoride to sulphur chloride pentafluoride, though the quantity of sulphur chloride pentafluoride is very small. The behaviour is consistent with equations 5.3 and 5.4.

$$F^-.SF_4(ads) \longrightarrow SF_5^-(s) \qquad \text{Eq 5.3}$$

$$SF_5^-(s) + ClF(g) \longrightarrow SF_5Cl(g) \qquad \text{Eq 5.4}$$

Unlike the results obtained when chlorine monofluoride is admitted to sulphur tetrafluoride pretreated catalyst, the results obtained in chapter 4 show that the admission of sulphur tetrafluoride to mercury(II) fluoride pretreated with $[\,^{36}Cl\,]$– chlorine labelled chlorine monofluoride has no effect on the activity of the solid and no sulphur chloride pentafluoride is obtained when this reaction is attempted with non radioactive material. Therefore, the formation of sulphur chloride pentafluoride according to

$$ClF(g) + F^-(s) \longrightarrow ClF_2^-(s) \qquad \text{Eq 5.5}$$

$$ClF_2^-(s) + SF_4(g) \longrightarrow SF_5Cl(g) \qquad \text{Eq 5.6}$$

does not occur, that is, the permanently retained chlorine monofluoride does not participate to any extent in reaction with sulphur tetrafluoride to form sulphur chloride pentafluoride.

In previous work involving caesium fluoride, Kolta and coworkers stated that, no displacement of chlorine monofluoride retained by caesium fluoride occured, from its complex $CsClF_2^-$, by admission of sulphur tetrafluoride to caesium fluoride pretreated with chlorine monofluoride. However, the displacement of retained sulphur tetrafluoride on caesium fluoride, from its complex $CsSF_5^-$, by admission of chlorine monofluoride to caesium fluoride pretreated with sulphur tetrafluoride is observed. In the

context of Lewis acid– base reactions, Lewis stated that, the stronger Lewis acid will displace the weaker one from its complex[12]. The results obtained above for mercury(II) fluoride are in agreement with those obtained by Kolta and coworkers in the previous work. Since the reaction of chlorine monofluoride or sulphur tetrafluoride with either caesium fluoride or mercury(II) fluoride are Lewis acid– base reactions, it seems therefore that the displacement of sulphur tetrafluoride retained from its complex, pentafluorosulphate of caesium, is due to the Lewis acidity of chlorine monofluoride, that is chlorine monofluoride is a stronger Lewis acid than sulphur tetrafluoride.

The results presented in chapter 4 together with those in chapter 5 show that the formation of sulphur chloride pentafluoride by the reaction of strongly bonded chlorine monofluoride and sulphur tetrafluoride gas, Equation 5.6, or the reaction of strongly bonded sulphur tetrafluoride and chlorine monofluoride gas, equation 5.4, is improbable. This behaviour is analogous to that previously observed on caesium fluoride. However, the results presented in chapter 5 using the surface concentration of chlorine monofluoride and sulphur tetrafluoride by monitoring the activity of the surface during reaction of [^{36}Cl]– chlorine labelled chlorine monofluoride and sulphur tetrafluoride or [^{35}S]– sulphur labelled sulphur tetrafluoride and chlorine monofluoride, 1:1 mole ratio indicate that the formation of sulphur chloride pentafluoride is a true surface reaction involving adsorbed chlorine monofluoride and sulphur tetrafluoride. Therefore, the overall reactions involved during the formation of sulphur chloride pentafluoride at mercury(II) fluoride can be presented according to the following equations

$$F^-(s) + SF_4(g) \rightleftharpoons F^-.SF_4(ads) \qquad \text{Eq. 5.7}$$

$$F^-.SF_4(ads) \longrightarrow SF_5^-(s) \qquad \text{Eq. 5.8}$$

$$F^-(s) + ClF(g) \rightleftharpoons F^-.ClF(ads) \qquad \text{Eq. 5.9}$$

$$F^-.ClF(ads) \longrightarrow ClF_2^-(s) \qquad \text{Eq. 5.10}$$

$$F^-.SF_4(ads) + F^-.ClF(ads) \longrightarrow SF_5Cl + 2F^-(s) \qquad \text{Eq. 5.11}$$

Since the chlorofluorination of sulphur tetrafluoride by chlorine monofluoride is a base catalysed reaction, the active basic sites of mercury(II) fluoride are likely to be fluoride ions by which the reactants are adsorbed to form $F^-.SF_{4(ads)}$, which represents the surface adsorbed state of sulphur tetrafluoride, and $F^-.ClF_{(ads)}$, which represents the adsorbed state of chlorine monofluoride.

The results presented in chapter 4 indicates that there is significant retention of chlorine monofluoride by mercury(II) fluoride. Unlike caesium fluoride, the retained chlorine monofluoride at mercury(II) fluoride can be removed to some extent by evacuation of the solid at room temperature. However, the retained chlorine monofluoride at caesium fluoride cannot be removed to any extent by evacuation at room temperature. The results obtained in chapter 5 show that a high yield of sulphur chloride pentafluoride is obtained with mercury(II) fluoride pretreated with

hexafluoracetone. The repeated addition of the mixture of 1:1 mole ratio using the same sample of catalyst does not affect the yield. The results presented in chapter 5 indicate that the reaction of chlorine monofluoride with sulphur tetrafluoride over mercury(II) fluoride pretreated with hexafluoracetone to form sulphur chloride pentafluoride proceed very rapidly. Further more a high yield is obtained within a time shorter than that when caesium fluoride is used. Therefore from these observations it can be suggested that mercury(II) fluoride pretreated with hexafluoroacetone would be a better catalyst than caesium fluoride for the chlorofluorination of sulphur tetrafluoride by chlorine monofluoride.

The work reported by Mews and coworkers suggests that there is no interaction between mercury(II) fluoride and chlorine monofluoride[73]. This observation is not consistent with the results obtained in this work. It is clear from radiotracer study used in this work that there is a strong interaction between mercury(II) fluoride and chlorine monofluoride. The data presented in chapter 4 indicate that there is a significant retention of chlorine monofluoride by mercury(II) fluoride and that the retained species cannot be removed by evacuation at room temperature.

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